Organic Chemistry Part 2

CHAPTER 7

7 Organic Compounds with Functional Groups Containing Nitrogen

7.1 INTRODUCTION

Amines are derived by replacing one or more H atoms of NH_3 molecule by alkyl (R) or aryl (Ar-) groups, e.g., $CH_3—NH_2$, $Ph—NH_2$, Me—NH—Me, Me_3N.

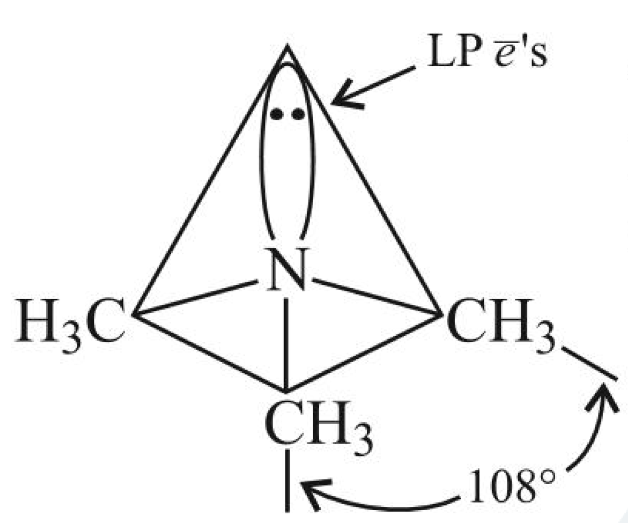
(a) Occurence: They occur in nature in proteins, vitamins, hormones, and alkaloids. Synthetic examples include drugs, dyes, and polymers.

(b) Uses: Adrenaline and ephedrine are biologically active compounds, both contain 2° amine group, and they are used to increase blood pressure. A synthetic amino compound, novocain is used as an anaesthetic in dentistry.

Antihistamine drug, Benadryl, contains a 3° amino group. 4° ammonium salts are used as surfactants. Diazonium salts are used as intermediates in the preparation of dyes and other important aromatic compounds.

(c) Structures of amines: In amines, N atom is sp^3-hybridised, with pyramidal geometry. Each of the three sp^3-hybridised orbitals of N atom overlaps with the orbitals of H or C atom depending on the structure of the amines.

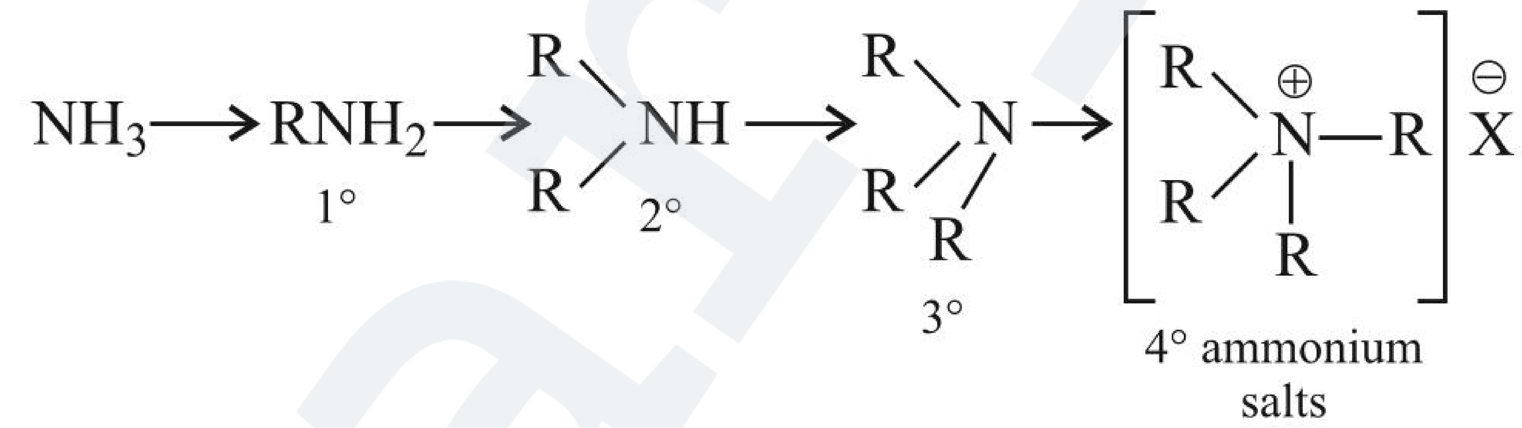
The fourth orbital of N in all amines contains LP $\bar{e}$'s due to which the C–N–H or C–N–C angle is less than 109.5°; for example, in trimethyl amine, angle is 108°, as shown in Fig. 7.1.



Three σ-bonds (N—C), formed by the overlap of sp^3 N with sp^3 C.
1LP $\bar{e}$'s in sp^3 of (N).

Fig. 7.1. Pyramidal shape of $Me_3\ddot{N}$

(d) Classification: They are classified as 1°, 2°, and 3° amines and 4° ammonium salts, depending on the number of H atoms replaced by R or Ar groups in NH_3 molecule, e.g.,



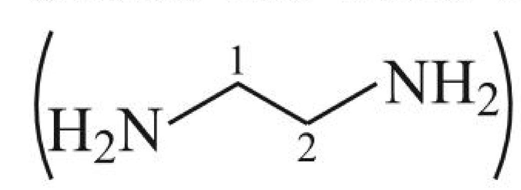
When all the alkyl or aryl groups are same, amines are called simple, and they are called mixed when they are different.

(e) Nomenclature:

i. **IUPAC system:**

Amines are named alkanamines, derived by the replacement of '*e*' of alkane by the word amine, e.g., CH_3NH_2 is named methanamine.

In case more than one amino group are present at different positions in the parent chain, their positions are mentioned by giving numbers to the C atom bearing (—NH_2) groups and suitable prefix such as di, tri, etc., is attached to the amine. The word '*e*' of alkane is retained, e.g.,



is named ethane-1,2-diamine.

ii. **Common name:** An aliphatic amine is named by prefixing alkyl group to amine, i.e., alkylamine as one word, e.g., methylamine. 2° and 3° amines, containing same two or more groups, are named by prefix di or tri attached before the name of the alkyl group, e.g.,

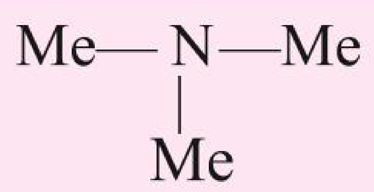
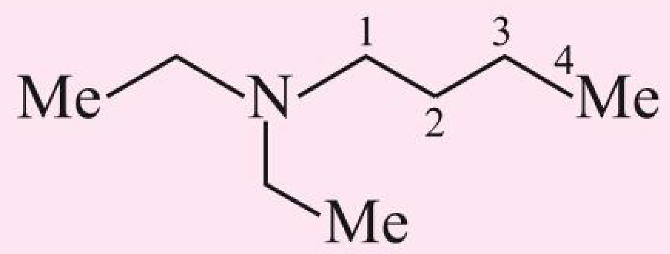
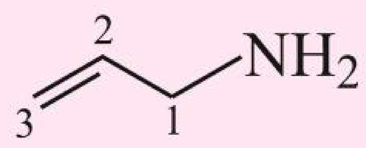
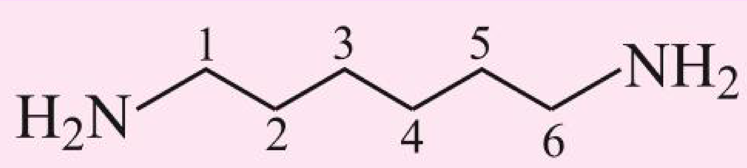
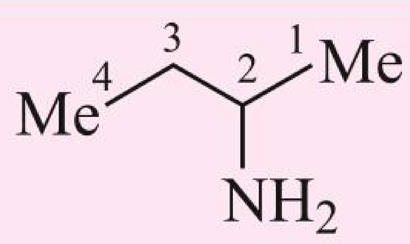
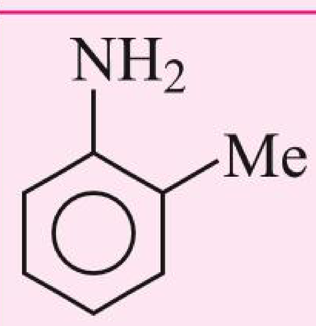
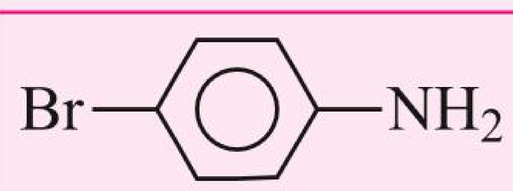
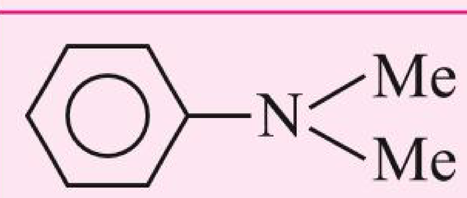
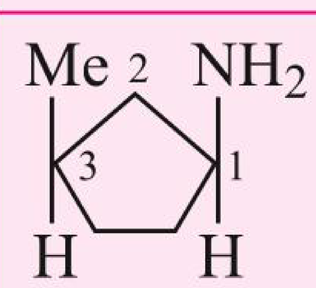
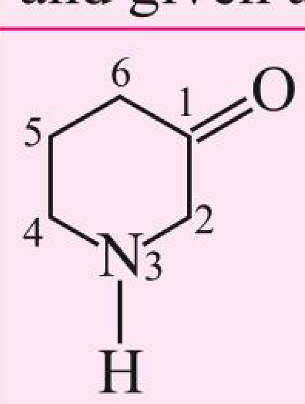
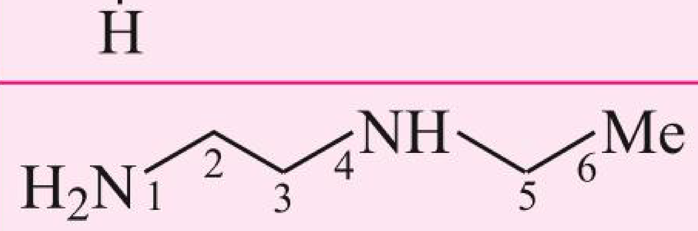
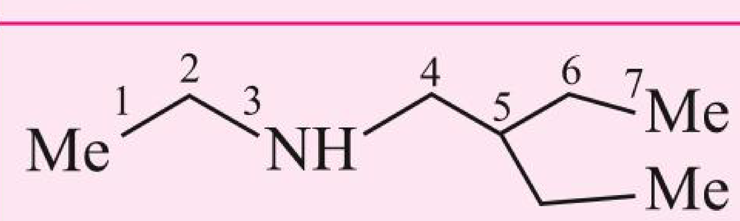
$\left(\begin{array}{c} \text{Et—N—Pr} \\ | \\ \text{Et} \end{array}\right)$ is named diethyl propyl amine.

iii. **Arylamines:** When an (—NH_2) group is directly attached to the benzene ring, the compound formed is called an arylamine; (Ph—NH_2) is the simplest example of arylamine; in the common system, it is called aniline, also an accepted IUPAC name.

According to IUPAC system, suffix '*e*' of arene is replaced with 'amine'. (Ph—NH_2) is named benzenamine.

Table 7.1 Nomenclature of some alkyl- and aryl amines

S. No.	Amine	IUPAC (or C.A. chemical abstract) name	Common name
1.	Me—NH_2 (1°)	Methanamine	Methylamine
2.	Et—NH_2 (1°)	Ethanamine	Ethylamine
3.	$\underset{3}{Me}\overset{NH_2}{\underset{2}{C}H}\underset{1}{Me}$ (1°)	Propan-2-amine	Isopropylamine

S. No.	Amine	IUPAC (or C.A. chemical abstract) name	Common name
4.	 (2°)	*N*-Methylethanamine	Ethylmethylamine
5.	 (3°)	*N*,*N*-Dimethylmethanamine	Trimethylamine
6.	 (3°)	*N*,*N*-Diethylbutan-1-amine	*N*,*N*-Diethylbutylamine
7.	 (1°)	Prop-2-en-1-amine	Allylamine
8.	 (2°)	*N*-Methyl prop-2-en-1-amine	*N*-Methylallylamine
9.	 (1°)	Hexane1,6-diamine	Hexamethylenediamine
10.	 (1°)	Butan-2-amine	*sec*-Butylamine
11.	$Ph–NH_2$ (1°)	Aniline or Benzenamine	Aniline
12.	 (1°)	2-Aminotoluene	*o*-Toluidine
13.	 (1°)	4-Bromobenzenamine or 4-Bromoaniline	*p*-Bromoaniline
14.	 (3°)	*N*,*N*-Dimethyl benzeneamine	*N*,*N*-Dimethyl aniline
15.	 (1°)	2-Aminobenzoice acid	*O*-Amino benzoic acid or Anthranilic acid
16.	 (1°)	*cis*-3-Methyl-1-cyclopentanamine	*cis*-3-Methyl-1-cyclopentylamine
17.	 (2°)	—	Aziridine (ethylenimine)
	Naming by aza (system): In aza system, N is counted in the chain as if it were C, but it is distinguished by the word 'aza' and given a position number.		
18.	 3-Azacyclohexanone		
19.	 1,4-Diazahexane		
20.	 5-Ethyl-3-azaheptane		

7.2 PHYSICAL PROPERTIES

a. Physical state: The lower aliphatic amines are gases with smell of fish. 1° amines up to three or four C atoms are liquids and higher ones are solids. Aniline and other arylamines are colourless but on storage become coloured due to atmospheric oxidation.

b. Solubility: Lower aliphatic amines are soluble in H_2O because they form H-bonding with H_2O. But solubility decreases with increase in molecular mass due to increase in size of the hydrophobic alkyl part. Higher amines are insoluble in H_2O.

Butan-1-ol is more soluble in H_2O than butan-1-amine due to greater EN of O atom than that of N atom (EN of O atom in alcohol is 3.5, whereas EN of N atom in amine is 3.0). Amines are soluble in organic solvents such as alcohol, benzene, and ether.

Alcohols are more polar than amines and form stronger intermolecular H-bonds than amines.

c. Boiling point: 1° amines form stronger intermolecular H-bonding between N atom of one and H atom of another molecule, than 2° amines, since 1° amines have two H atoms for H-bonding; that is why boiling points of 1° amines are greater than those of 2° amines of the same molar masses. Similarly, 2° amines form stronger intermolecular H-bonding than 3° amines, since 2° amines have one H atom for H-bonding due to the absence of H atom available for H-bond, whereas 3° amines do not form H-bonding. Thus, the boiling points of 2° amines are higher than those of 3° amines of the same molar masses.

The order of boiling points of isomeric amines is: 1° > 2° > 3° amines.

The intermoleular H-bonding in 1° and 2° amines is shown in Figs. 7.2 and 7.3.

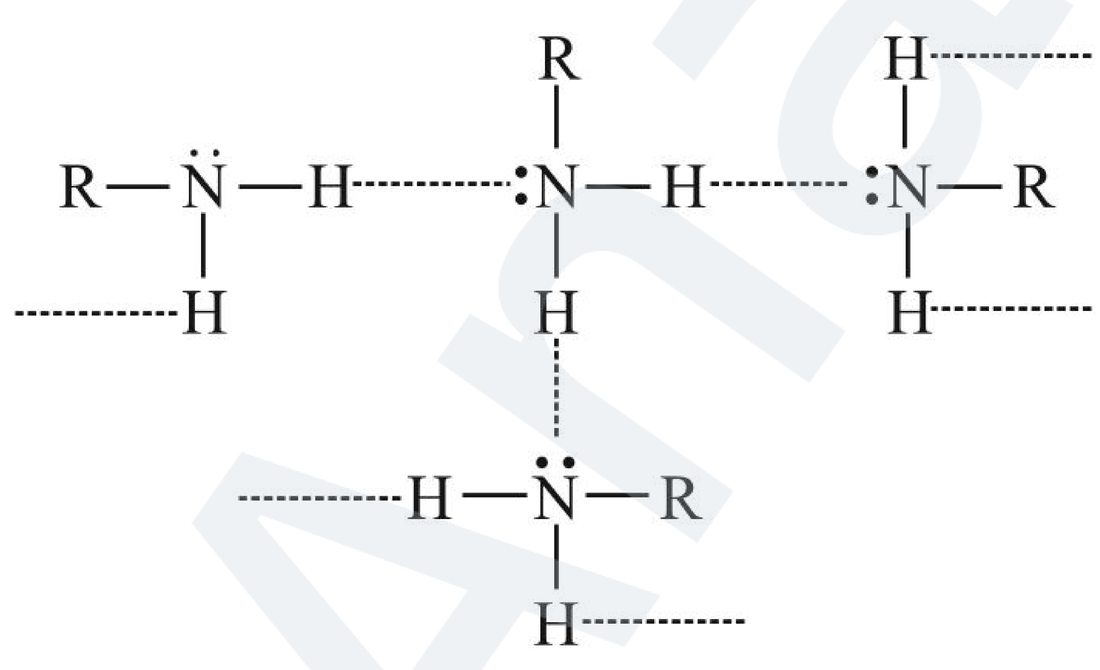


Fig. 7.2 Intermolecular H-bonding in 1° amines

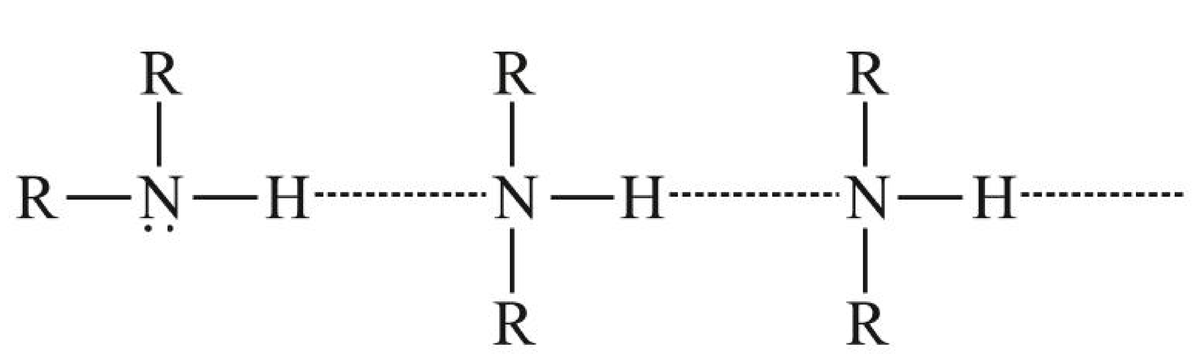
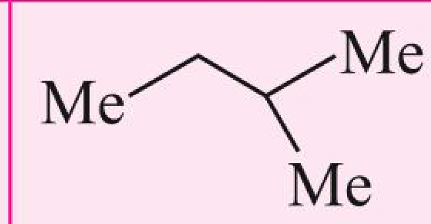


Fig. 7.3 Intermolecular H-bonding in 2° amines

Table 7.2 Comparison of boiling points of amines, alcohols, and alkanes of comparable molar masses

S.No.	Compound	Molar mass	Boiling point (K)
1.	n-$C_4H_9NH_2$ (1° amine)	73	350.8
2.	Et_2NH (2° amine)	73	329.3
3.	$EtNMe_2$ (3° amine)	73	310.5
4.	 (Alkane)	72	300.8
5.	n-C_4H_9OH (Alcohol)	74	390.3

d. Basic nature of amines:

Due to basic nature, they react with acids to form salts.

$$R-\ddot{N}H_2 + H-X \rightleftharpoons R-\overset{\oplus}{N}H_2X^{\ominus} \text{ (Salt)}$$

$$Ph-\ddot{N}H_2 + HCl \rightleftharpoons Ph\,\overset{\oplus}{N}H_3\,Cl^{\ominus} \text{ (Anilinium chloride)}$$

Amine salts on treatment with bases such as NaOH regenerate the parent amine.

$$R\,\overset{\oplus}{N}H_3\,X^{\ominus} + \overset{\ominus}{O}H \longrightarrow R\ddot{N}H_2 + H_2O + X^{\ominus}$$

Amine salts are soluble in H_2O but insoluble in organic solvents such as ether, which forms the basis for the separation of amines from the non-basic organic compounds insoluble in H_2O.

The reaction of amines with mineral acids to form ammonium salts shows that these are basic in nature. They behave as Lewis base due to the presence of LP $\overline{e}$'s on N atom. The basic character of amines can be explained in terms of their K_b or pK_b values. Larger the K_b or smaller the value of pK_b, stronger is the base. The pK_b value of NH_3 is 4.75. Aliphatic amines are stronger bases than NH_3, due to the +I effect of alkyl groups leading to high $\overline{e}$ density on the N atom. Aromatic amines are weaker bases than NH_3 due to the $\overline{e}$-withdrawing nature of aryl group.

Besides the inductive effect, solvation effect, steric hindrance, etc., affect the basic strength of amines.

i. Structure–basicity relationship of amines:

Basicity of amines depends upon their structure, upon the ease of formation of cation by accepting a proton from the acid. The more stable the cation relative to the amine, the more basic the amine is.

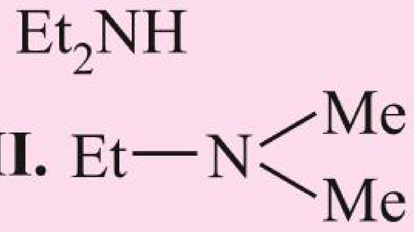
ii. Basic character of amines: See Chapter 4 (Part 1).

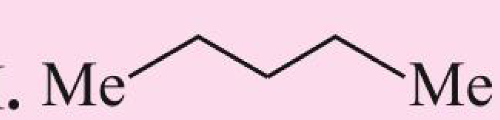
ILLUSTRATION 7.1

Give the decreasing order of boiling points for the following:

a. I. Et_2NH

II. 

III. 

b. I. 

II. 

III. 

Sol.

a. (II) > (I) > (III) (1° > 2° > 3° amine)

b. (II) > (III) > (I) (alcohol > amine > alkane)
H-bonding in alcohol is stronger than in amine since the EN of O > N. Alkane does not form H-bonding.

ILLUSTRATION 7.2

a. Give the decreasing order of solubility of the following in H_2O:
I. $PhNH_2$ **II.** Et_2NH **III.** $EtNH_2$

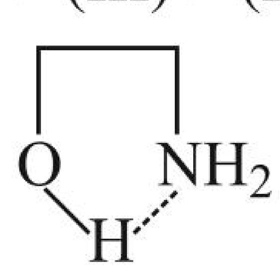
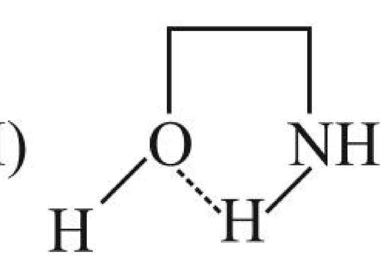
b. Give the decreasing order of boiling points of the following:
I. EtOH **II.** Me_2NH **III.** $EtNH_2$

c. Ethanolamine  can form two different interamolecular H-bonds. Write their structures. Which form is more stable?

Sol.

a. (III) > (II) > (I) (1° > 2° amine > arylamine). Arylamine is least soluble since it has a large hydrophobic part (phenyl group).

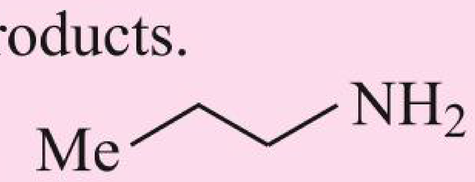
b. (I) > (III) > (II) (alcohol > 1° > 2° amine).

c. (I)  (II) 

(I) > (II). Since EN of O > N, its H-bond to N is stronger than the H-bond from N to O.

ILLUSTRATION 7.3

I. Arrange the following in the decreasing order of their basic strength:
a. i. $PhNH_2$ ii. $EtNH_2$ iii. Et_2NH iv. NH_3
b. i. $EtNH_2$ ii. $PhNH_2$ iii. NH_3 iv. $PhCH_2NH_2$ v. Et_2NH
c. i. $EtNH_2$ ii. Et_2NH iii. Et_3N iv. $PhNH_2$
d. i. $MeNH_2$ ii. Me_2NH iii. Me_3N iv. $PhNH_2$ v. $PhCH_2NH_2$

II. Complete the following acid–base reaction and name the products.
i.  $+ HCl \longrightarrow$
ii. $Et_3N + HCl \longrightarrow$

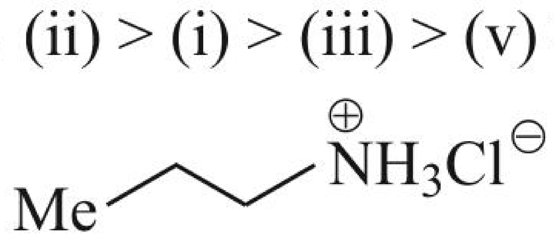
Sol. **I.**

a. Aliphatic 2° amine > Aliphatic 1° amine > NH_3 > Aromatic amine
(iii) > (ii) > (iv) > (i)

b. (v) > (i) > (iv) > (iii) > (ii)

c. (ii) > (iii) > (i) > (iv)

d. (ii) > (i) > (iii) > (v) > (iv)

II. i.  (Propanammonium chloride)

ii. $Et_3\,N^{\oplus}Cl^{\ominus}$ (Triethylammonium chloride)

7.3 PREPARATION OF AMINES

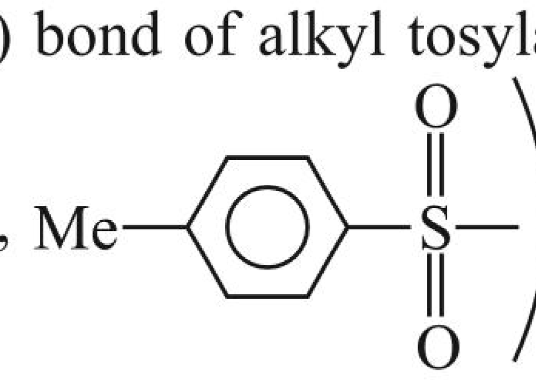
Amines are prepared by the following methods:

7.3.1 Reduction of Nitro Compounds

Nirtro compounds are reduced to amines by reduction with metals (Fe, Sn, or Zn) in dil. HCl or $SnCl_2$ in HCl or by passing H_2 gas in the presence of finely divided Ni, Pt, or Pd. Reduction with Fe scrap and HCl is preferred because the $FeCl_2$ formed gets hydrolysed to give HCl during the reaction, and thus only a small amount of HCl is required for the initiation of the reaction. LAH does not reduce $PhNO_2$ to $PhNH_2$ but to (Ph—N═N—PH).

$$Ph—N{=}N—Ph \xleftarrow{LAH} \left[\begin{array}{c} R—NO_2 \\ \text{or} \\ Ph—NO_2 \end{array}\right] \xrightarrow{\begin{array}{c} H_2/Pt + EtOH \\ \text{or} \\ Sn + HCl \text{ or} \\ Fe + HCl \end{array}} \begin{array}{c} R—NH_2 \\ \text{or} \\ PhNH_2 \end{array}$$

7.3.2 Hofmann Ammonolysis Reaction (SN^2 Reaction)

The process of cleaveage of (C—X) bond of alkyl halide (RX) or (C—O) bond of alkyl tosylate (R—OTs) (—Ts) is *p*-toluene sulphonyl,  with NH_3 molecule is known as ammonolysis. The reaction is carried out in a sealed tube at 373 K. The 1° amine obtained behaves as a nucleophile and reacts further with RX to form 2° and 3° amines and finally 4° ammonium salt.

i. $\underset{\text{Nucleophile}}{H_3\ddot{N}} + R—X \xrightarrow{SN^2} R\overset{\oplus}{N}H_3 + \ddot{X}^{\ominus}$

The fairly acidic product $R\overset{\oplus}{N}H_3$ ($pK_a \cong 10.6$) exchanges an $H^{\oplus}$ with NH_3 liberating the free amine RNH_2.

ii. $R\overset{\oplus}{N}H_3 + NH_3 \rightleftharpoons RNH_2 + \overset{\oplus}{N}H_4$

iii. The nucleophilic RNH_2 reacts with more RX to give 2°, 3° amines, and some 4° salt resulting in a complex mixture.

iv. $RNH_2 + RX$

$$\xrightarrow{SN^2} X^{\ominus} + R_2\overset{\oplus}{N}H_2 \underset{}{\overset{NH_3}{\rightleftharpoons}} \overset{\oplus}{N}H_4 + R_2NH\ (2°)$$

$$R_2NH \xrightarrow[RX]{SN^2} R_3\overset{\oplus}{N}H + X^{\ominus} \overset{NH_3}{\rightleftharpoons} R_3N(3°) + \overset{\oplus}{N}H_4$$

$$R_3N \xrightarrow[SN^2]{RX} \underset{\text{(4° ammonium salt)}}{R_4\overset{\oplus}{N}} + X^{\ominus}$$

The yield of 1° amine can be increased by taking excess of NH_3 to encourage its collision with RX and to discourage collisions of RX with 1° and 2° amines.

Moreover, this method cannot be used for the preparation of aryl amine (unless benzene ring is activated by EWG at *o*- and *p*-positions, e.g., (—NO_2) group, since ArX is much less reactive than RX towards SN reaction.

7.3.3 Reduction of Nitriles

Reduction of nitriles with LAH or catalytic hydrogenation gives 1° amines used for the ascent of amine series.

$$R{-}C{\equiv}N \xrightarrow[\text{H}_2\text{/Ni or Na (Hg)/EtOH}]{\text{LAH/EtOH or}} RCH_2NH_2$$

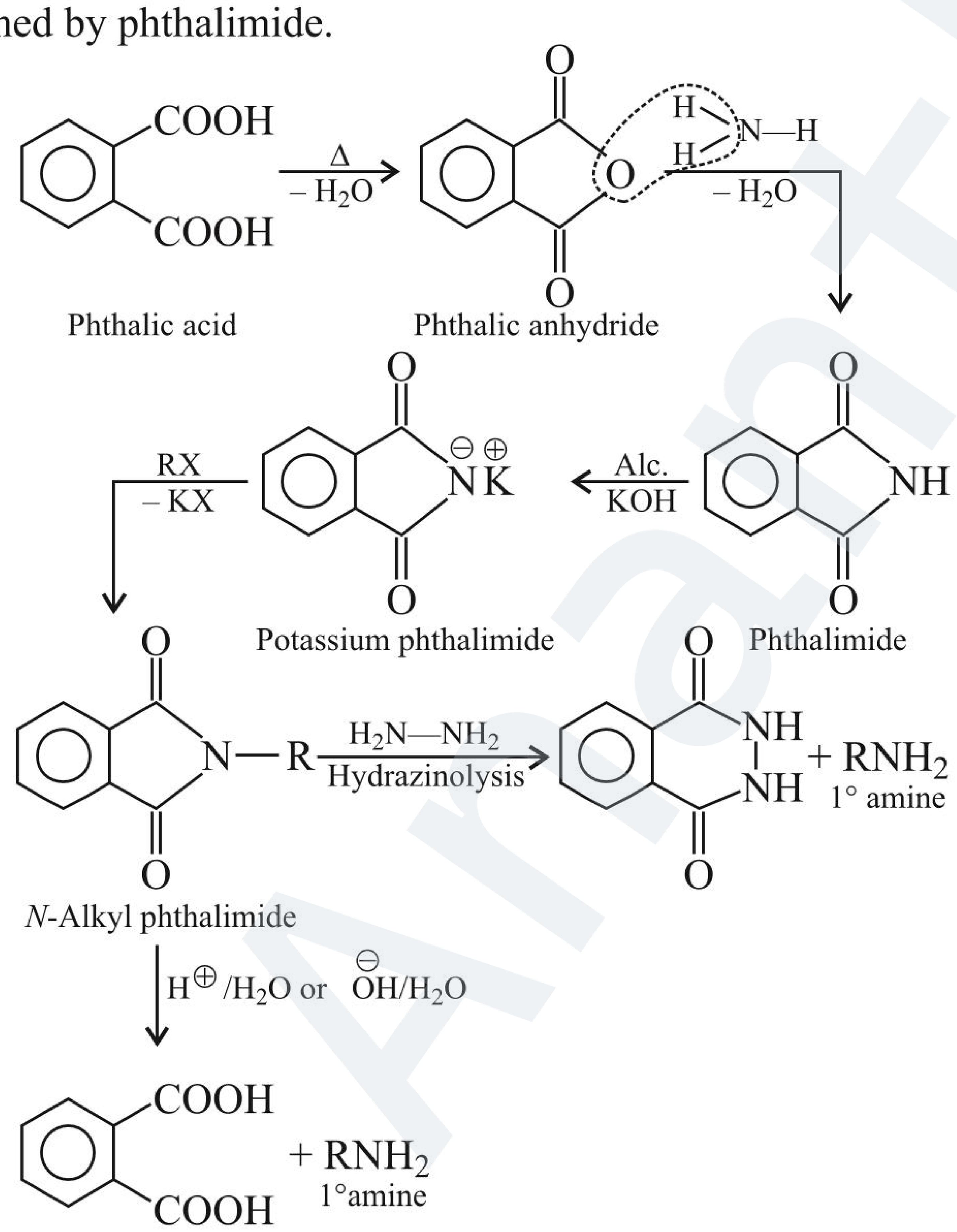
7.3.4 Reduction of Amides, Oximes, and Azides with LAH: All of Them with LAH give Amines

$$\left.\begin{array}{l} R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH_2 \text{ (Amide)}\\ R{-}CH{=}N{-}OH \text{ (Oxime)}\\ RCH_2N_3 \text{ (Azides)}\end{array}\right] \xrightarrow[\text{(ii) } H_2O]{\text{(i) LAH}} RCH_2NH_2$$

$$RCH_2N_3 \xrightarrow{H_2\text{–Pd/C}} RCH_2NH_2 + N_2$$

7.3.5 Gabriel Phthalimide Synthesis

This reaction is used for the preparation of 1° aliphatic amine and 1° aromatic amine (containing EWG at *o*- and *p*-positions, e.g., (—NO_2) group). Phthalimide on treatment with ethanolic KOH forms potassium salt of phthalimide which on heating with RX followed by either alkaline hydrolysis or hydrazinolysis with hydrazine ($H_2N.NH_2$) produces the corresponding 1° amine. 1° aromatic amine (except those containing EWG at *o*- and *p*-positions, e.g., (—NO_2) group) cannot be synthesised by this method because ArX does not undergo SN reaction with anion formed by phthalimide.



7.3.6 Hofmann Bromamide Degradation Reaction

See Section 6.16.1.

Amides on reaction with Br_2 in an aqueous or ethanolic solution of NaOH give 1° amine with one C atom less than that present in the amide.

$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH_2 + Br_2 + 4NaOH \longrightarrow R{-}NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

7.3.7 Lossen Rearrangement Reaction

See Section 6.16.2.

Hydroxamic acid on reaction with base followed by hydrolysis gives 1° amine.

$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH{-}OH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } \overset{\ominus}{O}H} RNH_2 + CO_2$$

7.3.8 Curtius Rearrangement Reaction

See Section 6.16.3.

Acid azides on heating followed by hydrolysis give 1° amine.

$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}N_3 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } \Delta} RNH_2 + CO_2$$

7.3.9 Claisen–Schmidt Rearrangement Reaction

See Section 6.16.4.

Carboxylic acid on reaction with hydrazoic acid in the presence of H_2SO_4 gives acid azide which on heating followed by hydrolysis gives 1° amine.

$$RCOOH \xrightarrow[H_2SO_4]{HN_3} R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}N_3 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } \Delta} RNH_2 + CO_2$$

Illustration 7.4

Write chemical reactions for the following:

a. Reaction of ethanolic NH_3 with EtBr.

b. Ammonolysis of benzylbromide and reaction of amine so formed with 2 mol MeBr.

Sol.

a. $$\underset{\text{Bromo-ethane}}{Et{-}Br} \xrightarrow{NH_3} \underset{\text{Ethanamine}}{Et{-}NH_2} \xrightarrow{Et-Br} \underset{N\text{-Ethyl ethanamine}}{Et_2NH} \xrightarrow{Et-Br} \underset{N,N\text{-Diethyl ethanamine}}{Et_3N}$$

b. $$\underset{\text{Benzyl-bromide}}{PhCH_2Br} \xrightarrow{NH_3} \underset{\text{Benzylamine}}{PhCH_2NH_2} \xrightarrow{2\ MeBr} \underset{N,N\text{-Dimethyl phenyl methanamine}}{PhCH_2{-}\overset{\overset{\displaystyle Me}{|}}{N}{-}Me}$$

Illustration 7.5

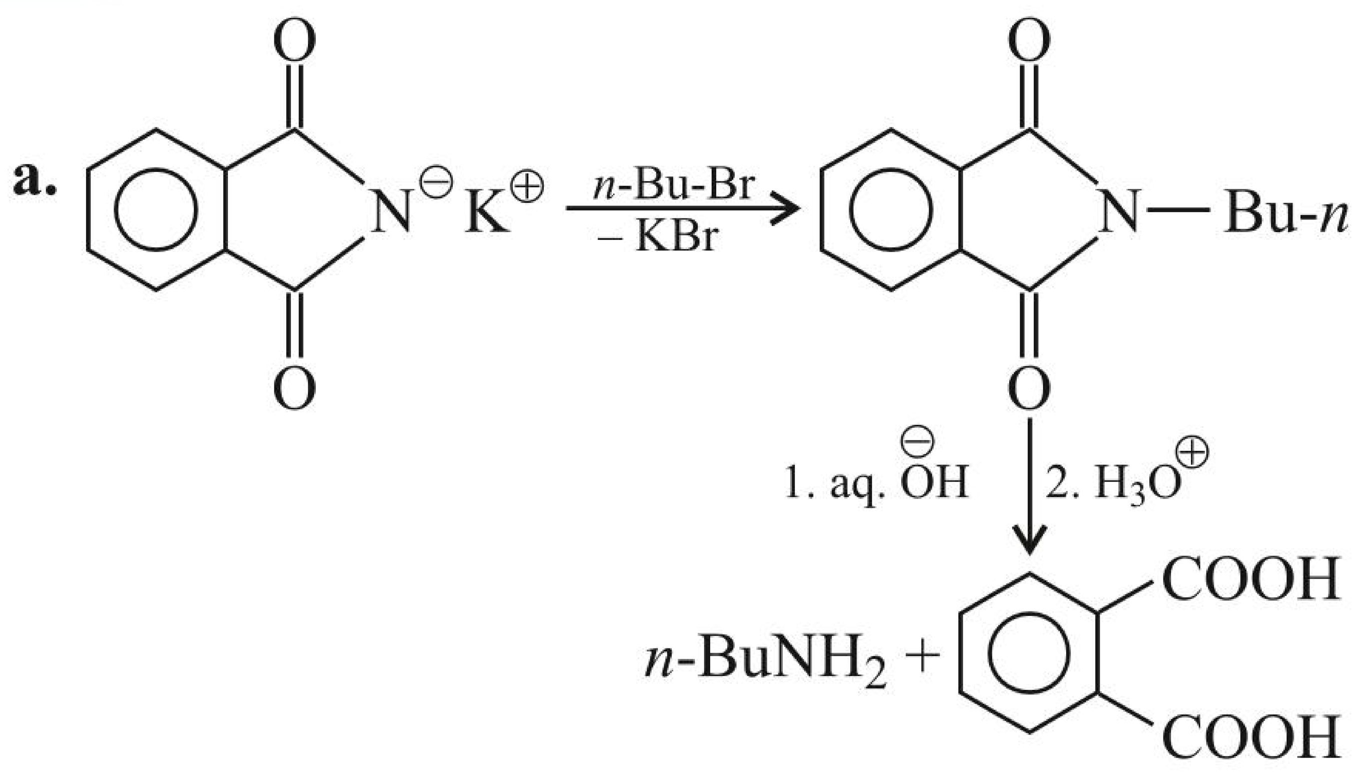
a. Prepare *n*-butylamine by Gabriel synthesis.

b. Which of the following cannot be prepared by Gabriel method from their corresponding halides or tosylates.

I. *t*-Butylamine, **II.** Neopentylamine,
III. Diethylamine, **IV.** *p*-Toluidine,
V. *m*-Nitroaniline.

Sol.

a.



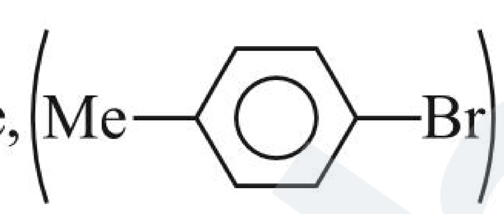
b. Halides or tosylates which are unreactive in SN^2 cannot be used.

(I) to (VI) cannot be prepared but (VII) to (IX) can be prepared.

I. It cannot be prepared since $Me_3C—X$ is 3° halide.

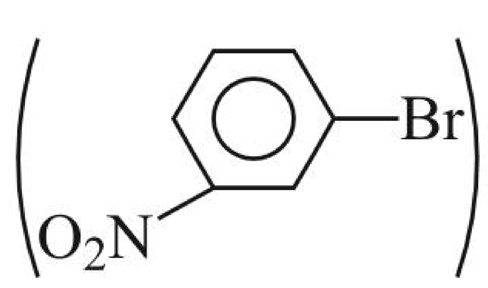
II. It cannot be prepared since $Me_3C—CH_2—X$ is neopentyl halide and does not undergo SN^2 reaction due to steric hindrance.

III. It cannot be prepared since 2° amine gives poor yield due to elimination.

IV. It cannot be prepared, since aryl halide, 

is not activated by EDG (Me group). ArSN reaction takes place only when the benzene ring is activated by EWG present at *o*- and *p*-positions.

V. It cannot be prepared, since EWG (—NO_2 group)



is present at *m*-position. ArSN reaction does not take place.

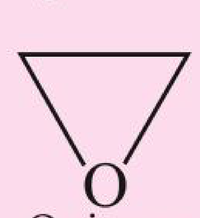
ILLUSTRATION 7.6

a. What kind of halides cannot be used to alkylate an amine?

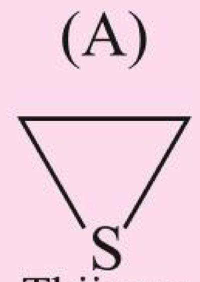
b. Identify (A) to (E).

$$PhSO_2Br + PrNH_2 \xrightarrow{—HCl} (A) \xrightarrow{KOH} (B) \xrightarrow{EtBr} (C) \xrightarrow{H_3O^\oplus} (D) + (E)$$

c. Complete the following reactions:

i.  $+ NH_3 \longrightarrow (B) \xrightarrow{(A)} (C) \xrightarrow{(A)} (D)$

Oxirane
(A)

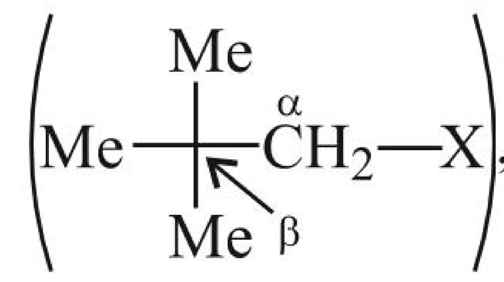
ii.  $+ NH_3 \longrightarrow (F) \xrightarrow{(E)} (G) \xrightarrow{(E)} (H)$

Thiirane
(E)

Sol.

a. I. 3° halides, because they form alkenes on elimination.

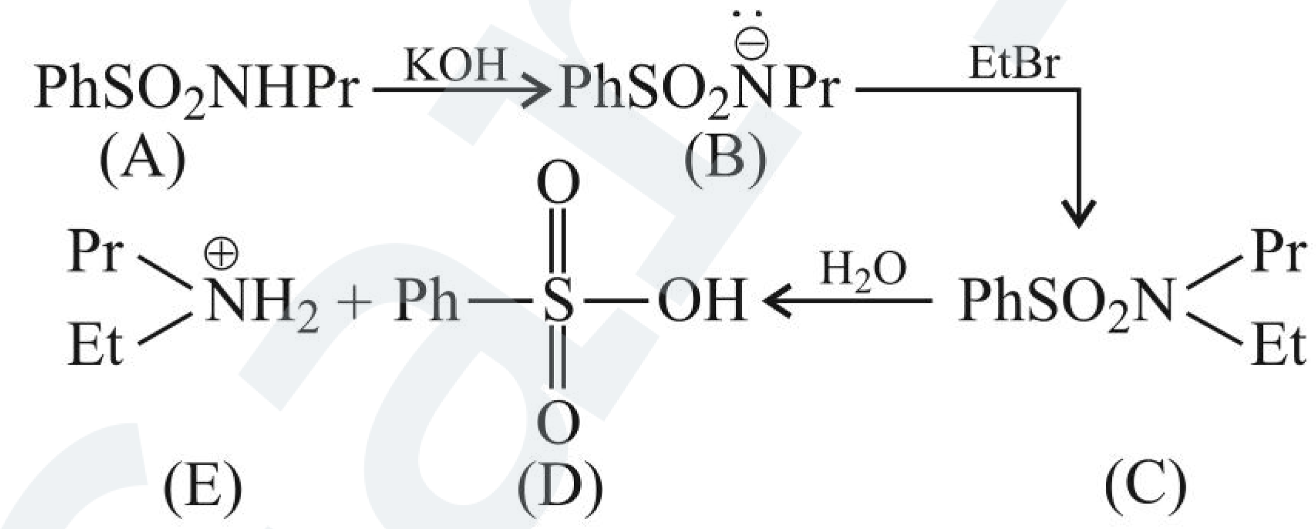
II. Halides with (β-alkyl) group as in neopentyl halides



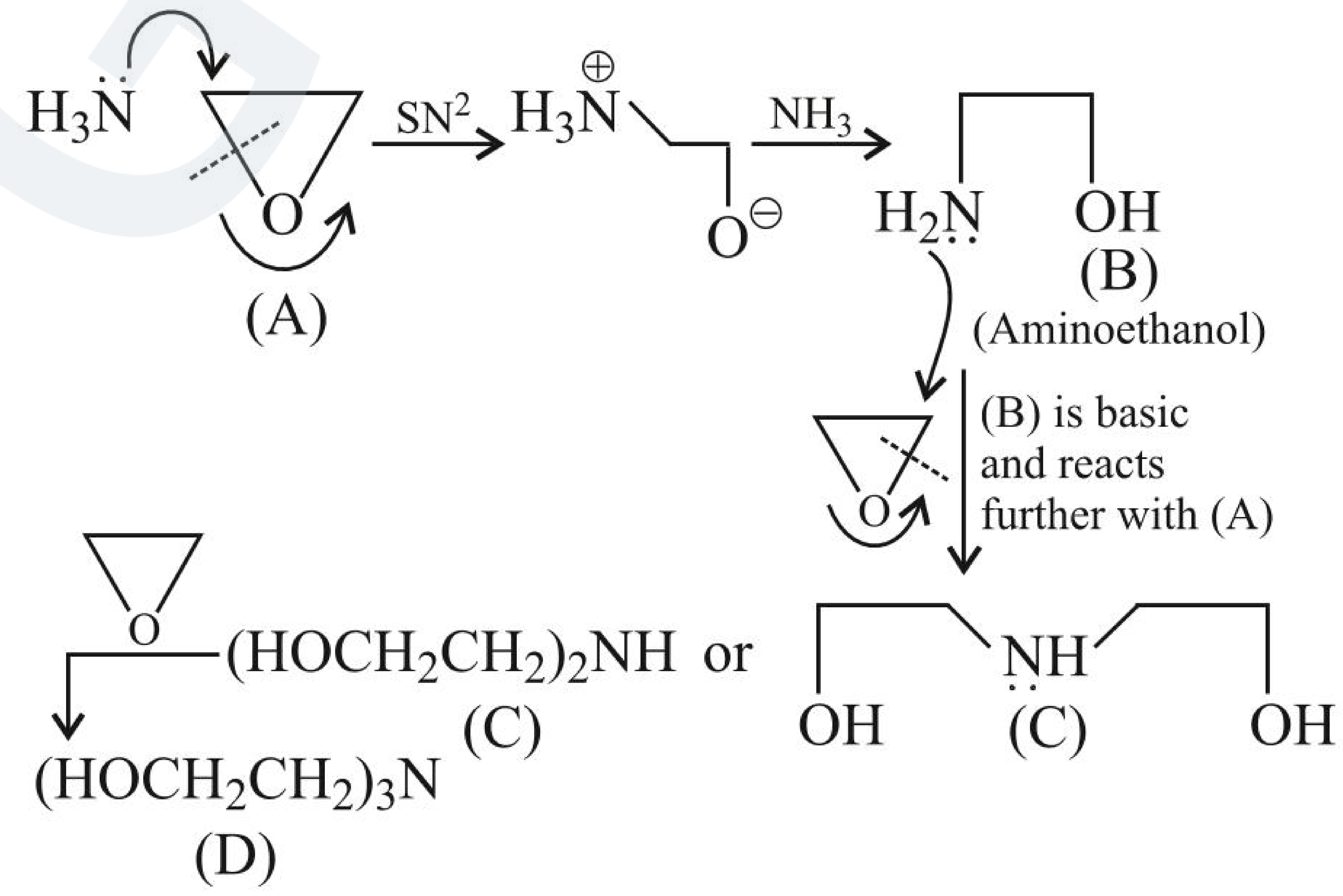
, due to steric hinderance.

III. Vinyl and aryl halides [unless activated by *o*- or *p*-substituted EWG, e.g., (—NO_2)], because they do not undergo ArSN reaction.

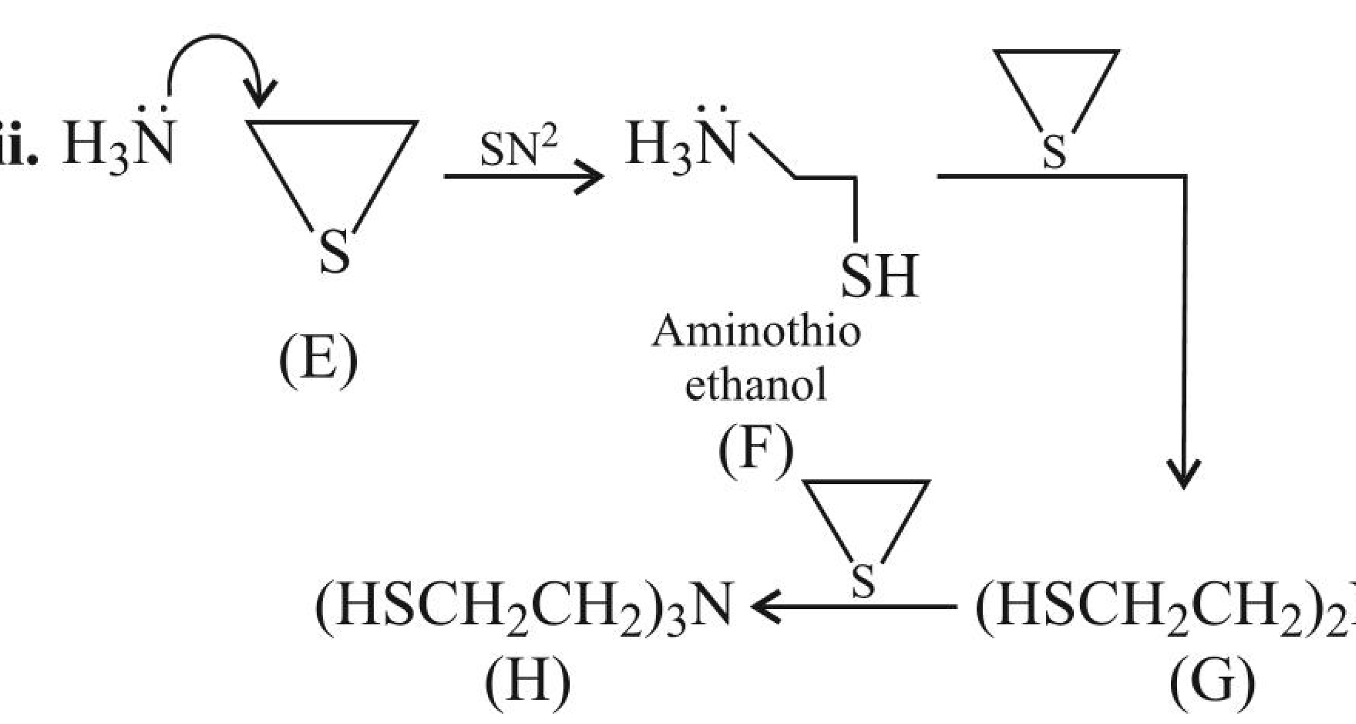
b.



c. i.



ii.



7.4 REDUCTIVE AMINATION OF CARBONYL COMPOUNDS

Aldehydes and ketones on reaction with NH_3 or 1° amine form imines (or Schiff base) which can be reduced on catalytic hydrogenation or using **sodium cyanoboro-hydride ($NaCNBH_3$).**

They form 1° and 2° amines as shown:

i. $RCH{=}O \xrightarrow[-H_2O]{H_2NH} \underset{\text{Imines}}{[RCH{=}NH]} \xrightarrow{H_2/Ni} \underset{\text{1° amine}}{RCH_2NH_2}$

ii. $R_2C{=}O \xrightarrow[-H_2O]{H_2NH} \underset{\text{Imines}}{[R_2C{=}NH]} \xrightarrow{H_2/Ni} \underset{\text{2° amine}}{R_2CHNH_2}$

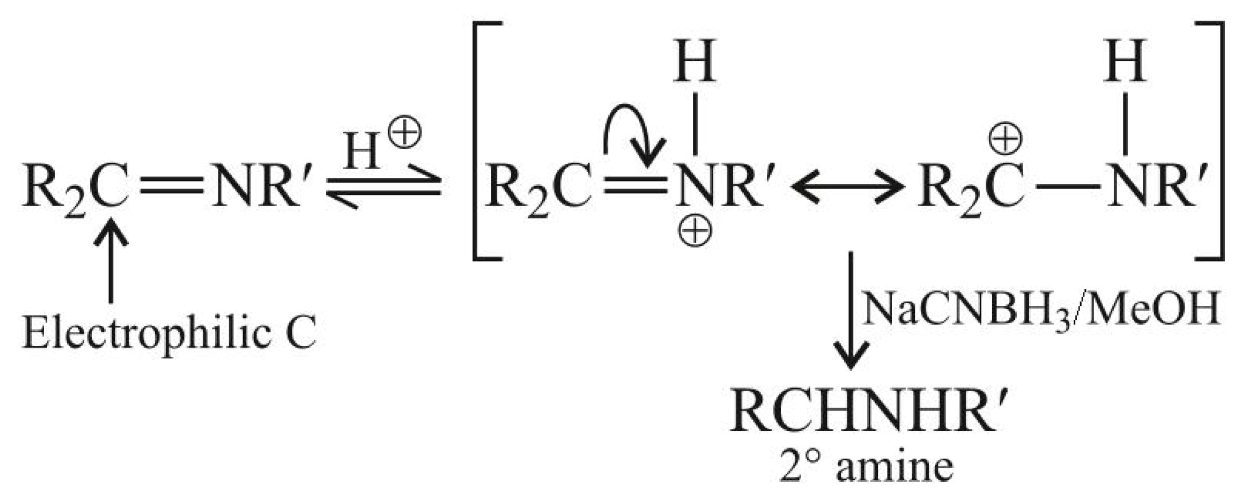
iii. $RCH{=}O \xrightarrow[-H_2O]{H_2NR'} \underset{\text{Substituted imines}}{[RCH{=}NHR']} \xrightarrow{H_2/Ni} \underset{2^\circ\text{ amine}}{RCH_2NHR'}$

Reduction of imine is more rapid than that of the starting carbonyl compound.

7.4.1 With ($NaCNBH_3$)

Since the $\bar{e}$-withdrawing (—CN) group retards $\overset{\ominus}{H}$ (hydride ion) donation, the reactant aldehyde or ketone $\left(\rangle C{=}O\right)$ is reduced by $NaCNBH_3$ more slowly than it reacts with amine to form imines.

The protonated imine, iminium ion formed at the pH of the reaction medium, is an electrophile and is rapidly reduced.



7.4.2 Advantage of Reductive Amination

Reductive amination produces the same kind of products as does the reaction of amines with RX. However, the reductive-amination is more easily controlled. When a ketone is used, the product has a *sec*-alkyl group; these amines are not easily synthesised by ammonolysis of R_2CHX which may undergo E2 elimination.

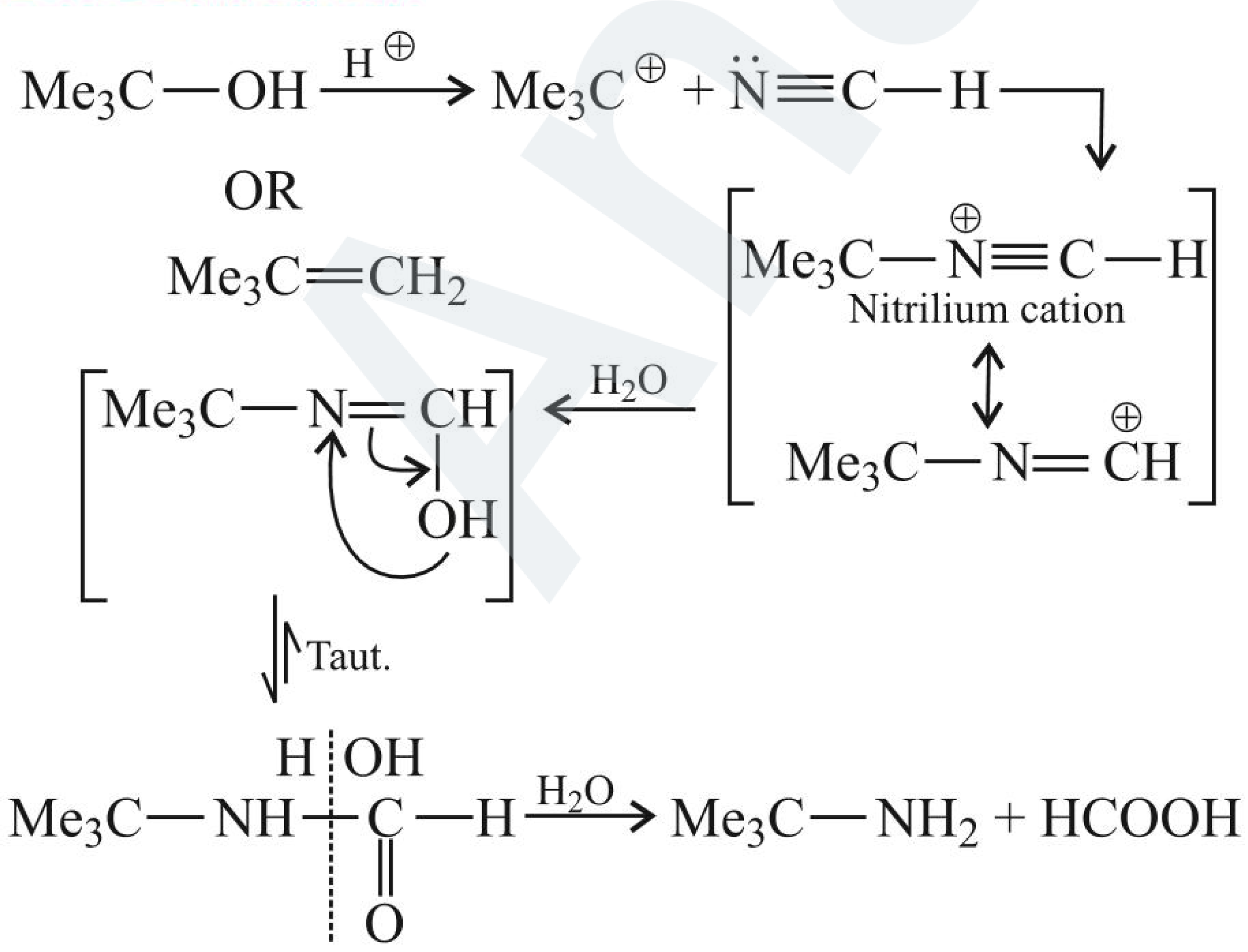
7.5 Ritter Reaction

It is used to prepare 1° amine containing 3° alkyl group (i.e., $Me_3C—NH_2$) which is difficult to synthesise by (i) Gabriel method, (ii) ammonolysis of RX, and (iii) reduction of N-containing compounds.

In Ritter reaction, $Me_3C—OH$ or $Me_2C{=}CH_2$ is reacted with conc. H_2SO_4 and HCN. In conc. H_2SO_4, these substrates are converted to $Me_3C^{\oplus}$ which then react with HCN.

$$Me_3C—OH + HCN + H_2SO_4 \longrightarrow Me_3C—NH_2 + HCOOH$$

7.5.1 Mechanism



(*N*-tert butyl formamide)

7.6 Leuckart Reaction

Ketones on reductive amination with $HCOONH_4$ (ammonium formate) or with DMF (dimethylformamide, $H—\overset{O}{\overset{\|}{C}}—NMe_2$) give amines, and this is called Leuckart reaction.

i. $R—\overset{O}{\overset{\|}{C}}—Me + HCOONH_4 \xrightarrow[180–200^\circ C]{\Delta} R—\underset{NH_2}{\underset{|}{CH}}—Me + H_2O + CO_2$

ii. $Et_2C{=}O + H—\underset{(DMF)}{\overset{O}{\overset{\|}{C}}}—NMe_2 \xrightarrow{\Delta} Et_2CH—NMe_2$

iii. 

7.7 Chemical Reactions

The difference of EN between N and H atoms and the presence of LP $\bar{e}$'s on N atom make amines reactive. 1°, 2°, and 3° amines differ in many reactions due to the presence of different number of H atoms attached to N atom.

1° and 2° amines are also methylated by heating HCHO and exccess of HCOOH at 100°C. This reaction is known as Eschweiler–Clark methylation.

7.7.1 Alkylation, Acylation, Benzoylation and Tosylation

7.7.1.1 Alkylation

Amines undergo alkylation with RX (MeI) and undergo complete methylation, and this is called exhaustive methylation, but with Me_2SO_4 (dimethyl sulphate) amines undergo monomethylation.

1° and 2° amines are also methylated by heating HCHO and excess of HCOOH at 100°C. This reaction is known as Eschweiler–Clarke methylation.

i. $\underset{1^\circ\text{ amine}}{RNH_2} + MeI \longrightarrow RNHMe \xrightarrow{MeI} RNMe_2 \xrightarrow{MeI} [R\overset{\oplus}{N}Me_3]I^{\ominus}$

ii. $\underset{2^\circ\text{ amine}}{R_2NH} \xrightarrow[MeI]{} R_2NMe \xrightarrow[MeI]{} [R_2\overset{\oplus}{N}Me_2]I^{\ominus}$

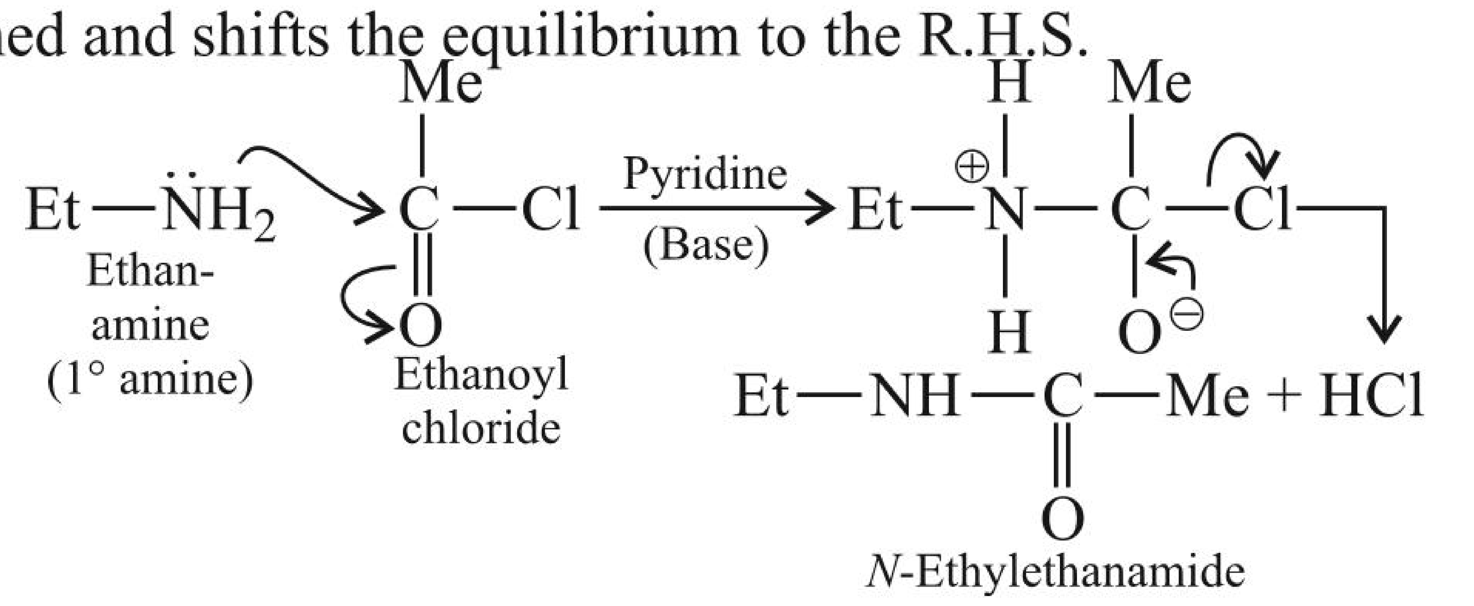
iii. $\underset{3^\circ\text{ amine}}{R_3N} \xrightarrow{MeI} [R_3\overset{\oplus}{N}—Me]I^{\ominus}$

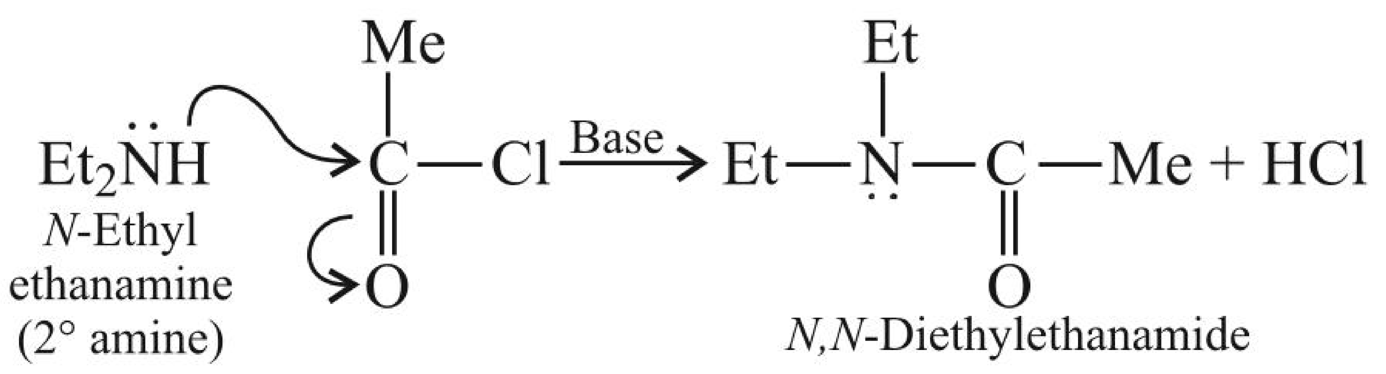
iv. $\underset{1^\circ\text{amine}}{RNH_2} + Me_2SO_4 \xrightarrow{NaOH} RNHMe$

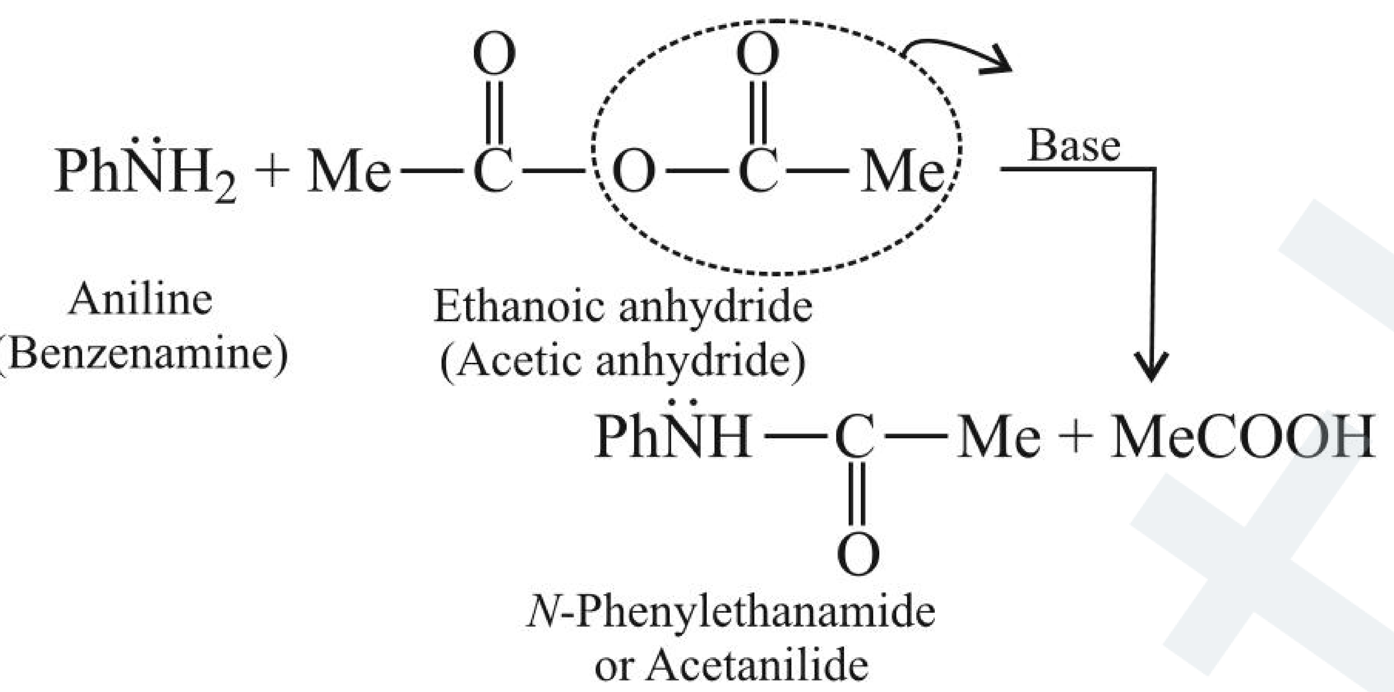
v. $C_2H_5NH_2 + CH_2{=}O + HCOOH \rightarrow C_2H_5NHMe + CO_2 + H_2O$

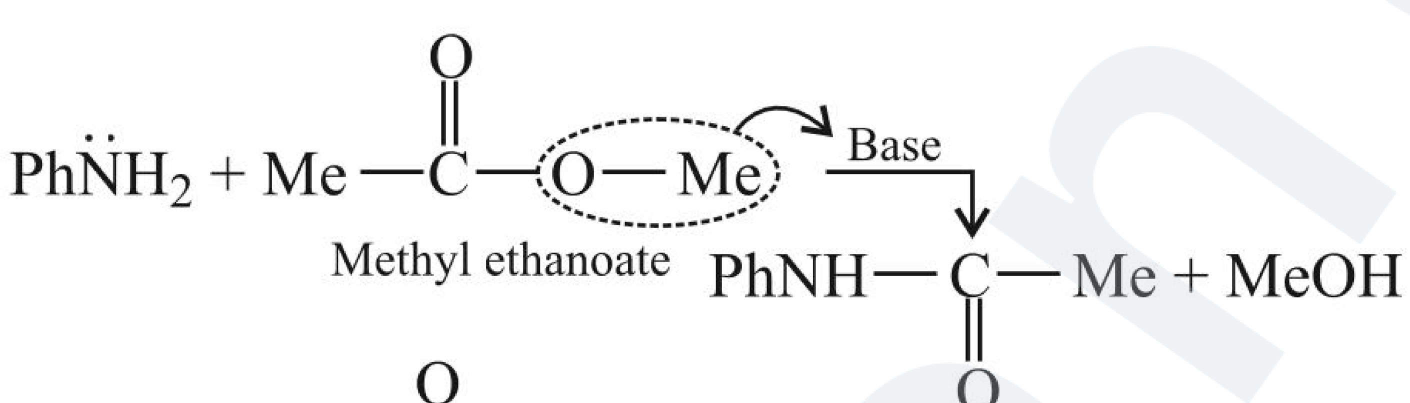
7.7.1.2 Acylation

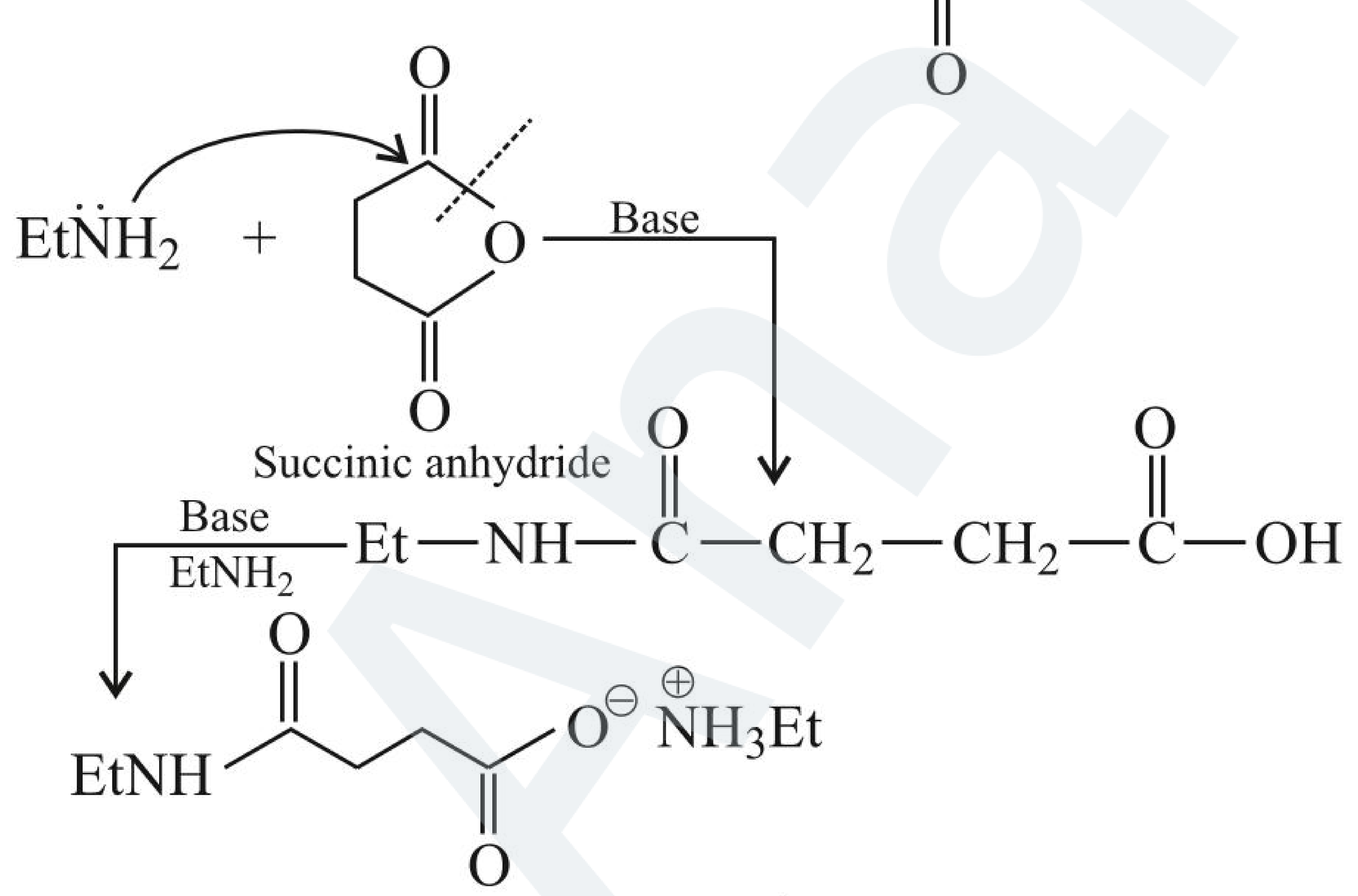
1° and 2° aliphatic and aromatic amines react with acid chlorides (RCOCl), anhydrides $\left(R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R\right)$, and esters (RCOOR′) by SN^2 reaction and the reaction is called acylation reaction. The reaction is carried out in the presence of a base stronger than amine, such as pyridine, which removes HCl so formed and shifts the equilibrium to the R.H.S.

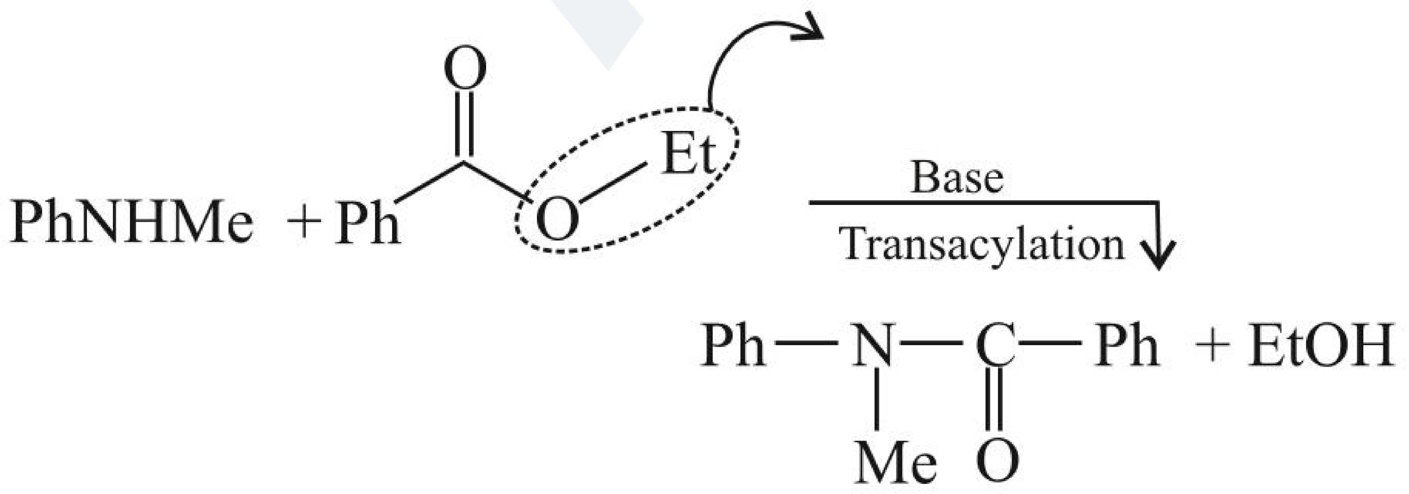
i. 

ii. 

iii. 

iv. 

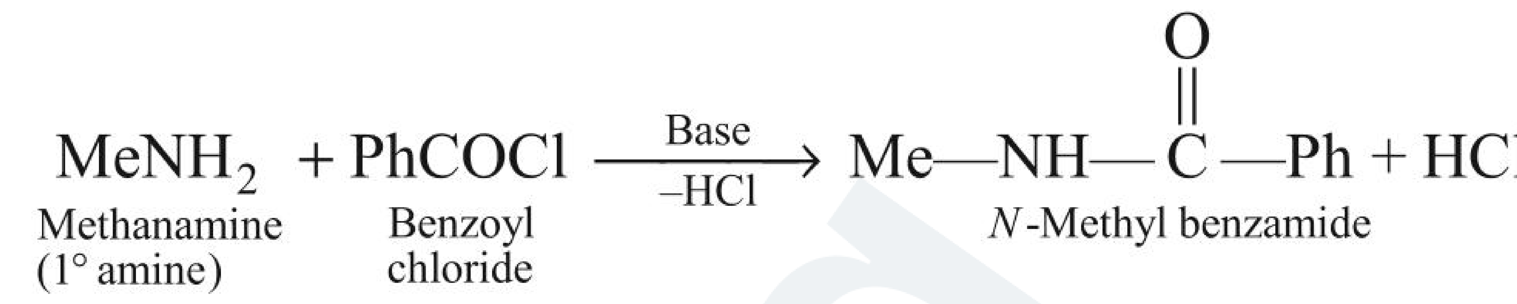
v. 

vi. 

vii. $PhNH_2 + RCOOH \longrightarrow \left[Ph\overset{\oplus}{N}H_3\right]\overset{\ominus}{C}OOR$ (Salt)

7.7.1.3 Benzoylation

Amines on reaction with benzoyl chloride (PhCOCl) give benzamide. This process is called **benzoylation reaction or Schotten–Baumann reaction**.



7.7.1.4 Tosylation

Amines on reaction with *p*-tolyl sulphonyl chloride gives tosyl derivative

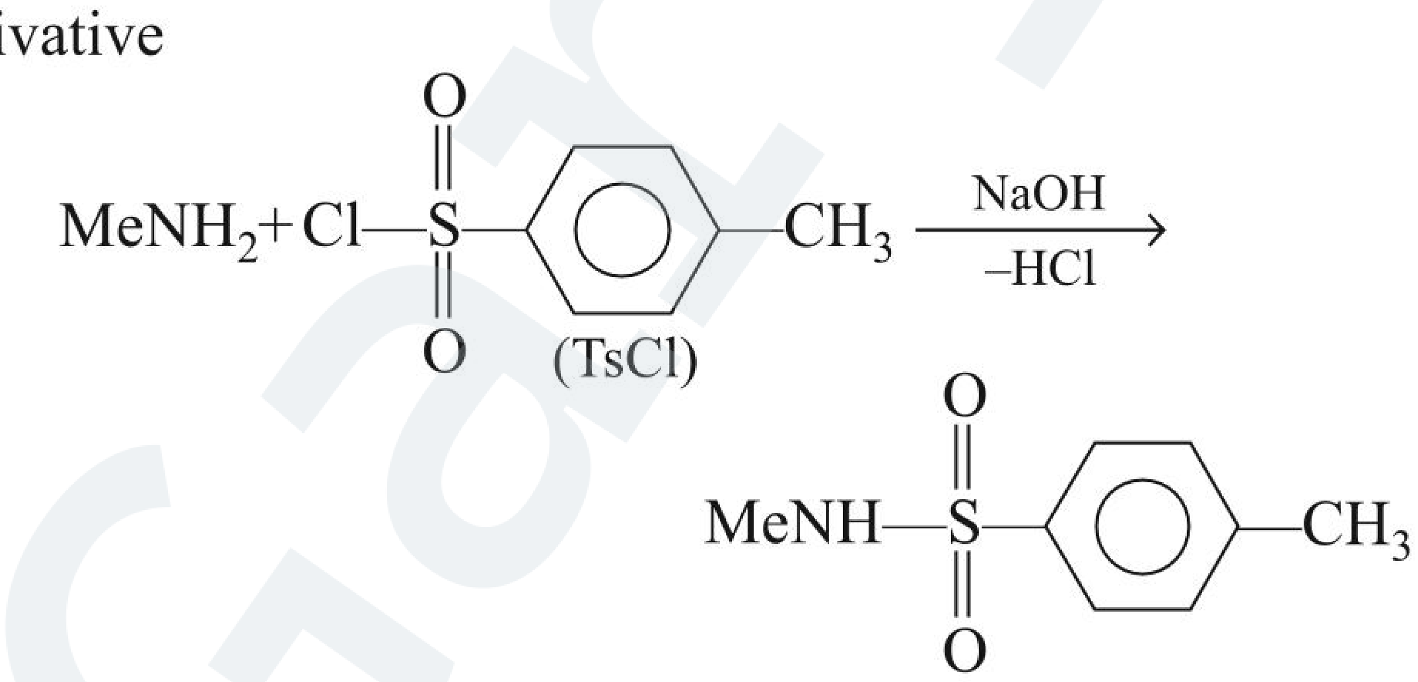


ILLUSTRATION 7.9

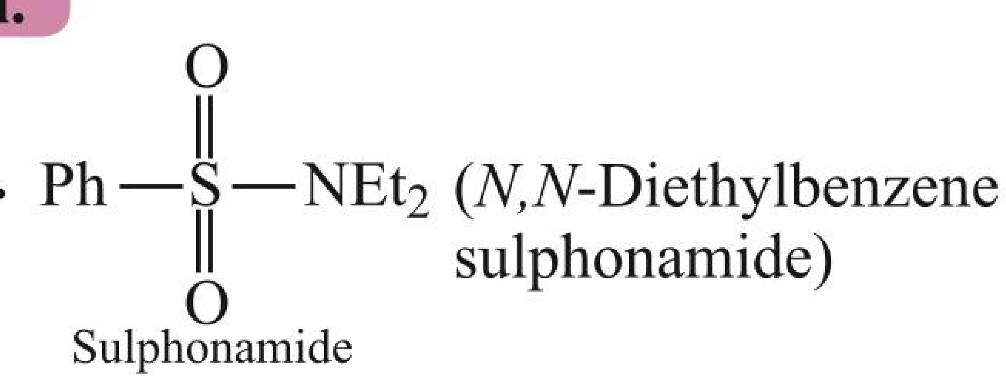
Complete the following reactions:

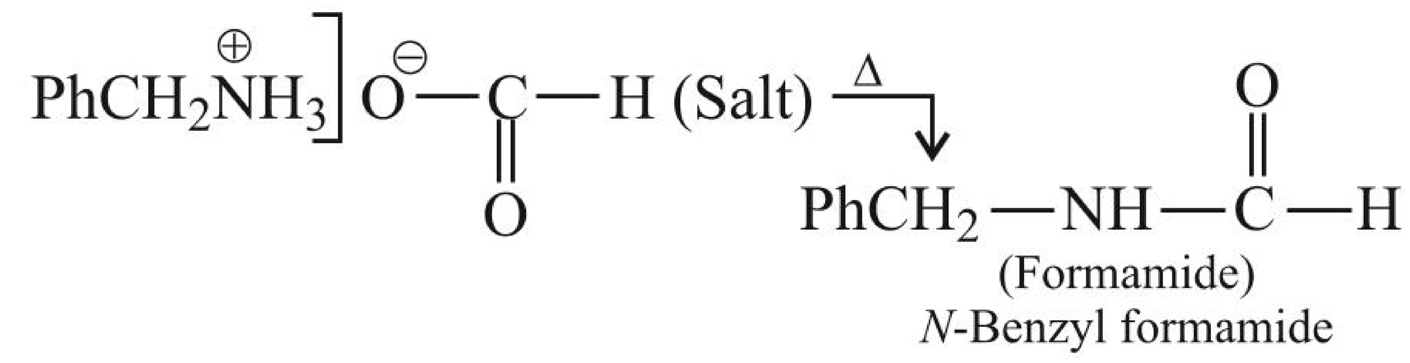
a. $Et_2NH + PhSO_2Cl \longrightarrow$

b. $PhCH_2NH_2 + HCOOH \xrightarrow{\Delta}$

c. $PhNH_2 + PhCHO \longrightarrow$

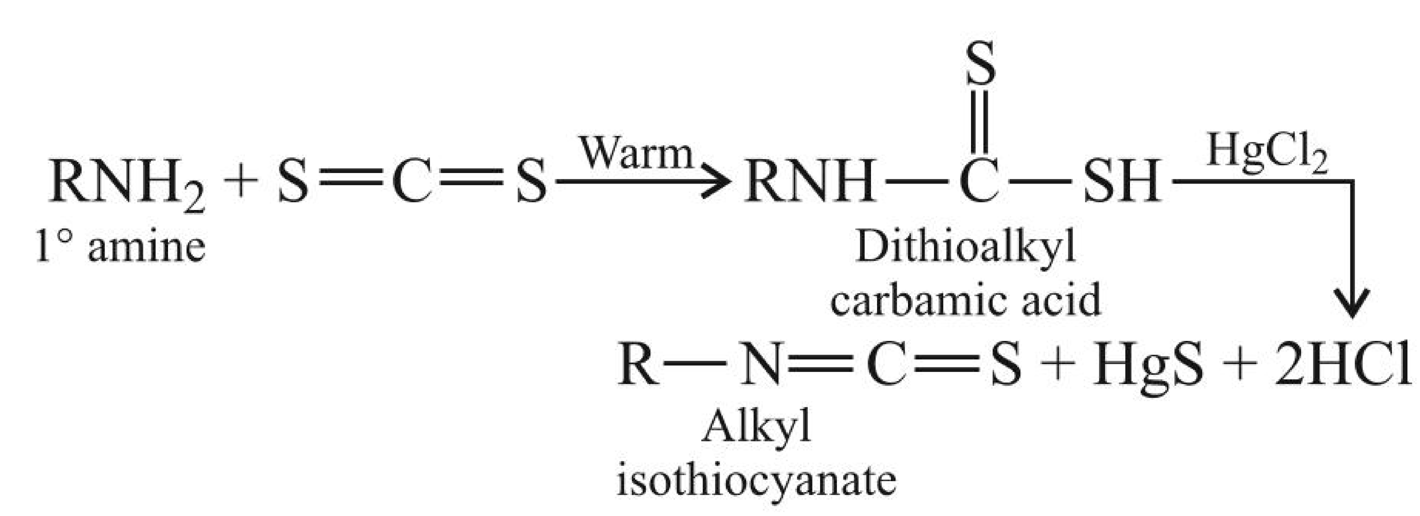
Sol.

a. 

b. 

c. $PhN(H_2 + O)=HC-Ph \rightarrow PhN=CH-Ph$ (Schiff's base)

7.8 Reaction with CS_2 and $COCl_2$ (Hofmann Mustard Oil Reaction) (Test for 1° Amines)

i. 

Alkyl isothiocyanates give a smell like that of mustard oil and this is used as a test for 1° amines.

ii. $$\begin{matrix}Ph-NH-H \\ Ph-NH-H\end{matrix} + S{=}C{=}S + 2KOH \xrightarrow{\Delta} \underset{N,N'\text{-Diphenyl thiourea}}{Ph-NH-\overset{\overset{S}{\|}}{C}-NHPh} + K_2S + H_2O$$

$$\xrightarrow{\text{Conc. HCl}} \underset{\text{Phenyl isothiocyanate}}{Ph-N{=}C{=}S} + Ph\overset{\oplus}{N}H_3Cl^{\ominus}$$

iii. $$PhNH_2 + Cl-\overset{\overset{O}{\|}}{\underset{\underset{Cl}{|}}{C}} \text{ (Phosgene or carbonyl chloride)} \longrightarrow Ph-N{=}C{=}O \text{ (Phenyl isocyanate)} + 2HCl$$

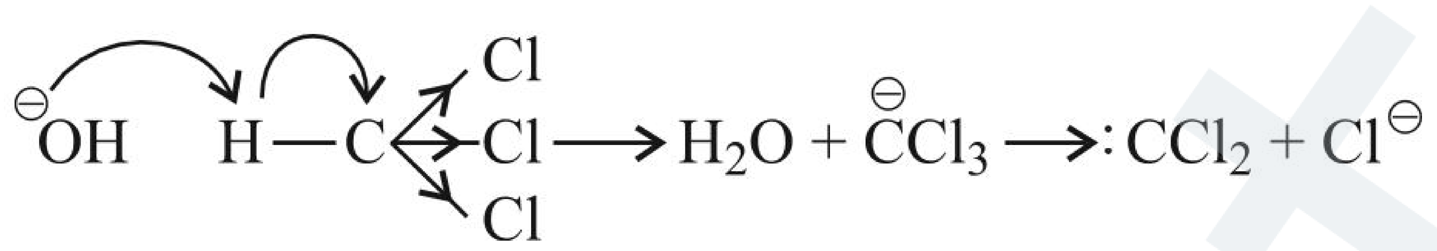
7.9 CARBYLAMINE REACTION (TEST FOR 1° ALIPHATIC OR AROMATIC AMINES)

It consists of heating a mixture of 1° aliphatic or aromatic amines and chloroform with alcoholic KOH solution. The reaction proceeds via carbene mechanism.

i. $$R-NH_2 + CHCl_3 + 3KOH \text{ (Alcoholic)} \xrightarrow{\Delta} R-\overset{\oplus}{N}{\equiv}C^{\ominus} + 3KCl + 3H_2O$$

ii. $$Ph-NH_2 + CHCl_3 + 3KOH \text{ (Alcoholic)} \xrightarrow{\Delta} Ph-\overset{\oplus}{N}{\equiv}C^{\ominus} + 3KCl + 3H_2O$$

Mechanism:



$$R-NH_2 + :CCl_2 \longrightarrow RN^{\oplus} \equiv C^{\ominus} + 2HCl$$

Isocyanides have a very offensive smell. So, this reaction is used to distinguish 1° amines.

7.10 REACTION WITH NITROUS ACID (TEST TO DISTINGUISH BETWEEN 1°, 2°, AND 3° AMINES)

Nitrous acid (HNO_2) is obtained *in situ* by the reaction of sodium nitrite ($NaNO_2$) with dil. HCl.

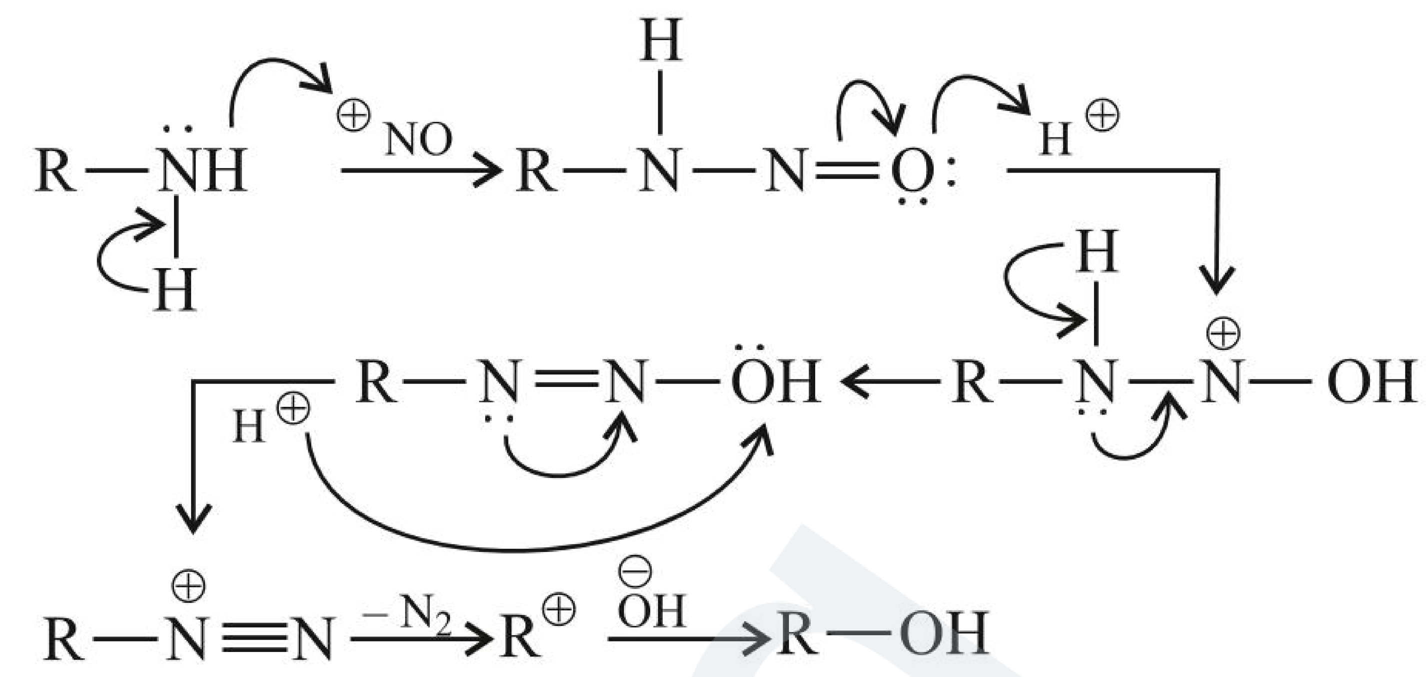
$$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$$

1° aliphatic amines react with HNO_2 to form aliphatic diazonium salts, which, being unstable, liberate N_2 gas quantitatively and alcohols. Quantitative evolution of N_2 is used in the estimation of amino acids and proteins.

$$R-NH_2 + HNO_2 \xrightarrow{NaNO_2 + HCl} \underset{\text{Diazonium chloride}}{[R-\overset{\oplus}{N}{\equiv}N]Cl^{\ominus}} \xrightarrow{H_2O} ROH + N_2 + HCl$$

7.10.1 Mechanism

HCl + $NaNO_2$ will give $NO^{\oplus}$ as an elecrophile (SE reaction).



7.10.2 Aromatic 1° Amines

$$PhNH_2 + HNO_2 + HCl \xrightarrow{273\text{–}278\ K} \underset{\text{(Benzene diazonium chloride)}}{[Ph-\overset{\oplus}{N}{\equiv}N]Cl^{\ominus}} + 2H_2O$$

The reaction for converting aromatic 1° amines with diazonium salts by treatment with a cold (273–278 K) solution of nitrous acid is called **Diazotisation**. If however, the temperature, rises above 278 K, the doiazonium salts decompose to form phenols.

$$Ph-\overset{\oplus}{N}{\equiv}NCl^{\ominus} + H_2O \xrightarrow[> 278\ K]{H^{\oplus}} PhOH + HCl + N_2$$

7.10.3 2° Amines (Aromatic and Aliphatic)

With HNO_2, they give *N*-nitroso amines, which being insoluble in dilute acids separate as yellow oily compounds. These *N*-nitroso amines on warming with a crystal of phenol and a few drops of concentrated H_2SO_4 form a green solution which when made alkaline with aqueous NaOH turns deep blue and then red on dilution. This reaction is called **Liebermann's nitroso reaction** and is used as a test for 2° amines.

$$R_2NH + HONO \longrightarrow \underset{\substack{N\text{-Nitroso dialkyl amine}\\ \text{(Yellow oil)}}}{R_2-N-N{=}O} + H_2O$$

$$\underset{\substack{N\text{-Methyl aniline}\\ \text{(Yellow oil)}}}{Ph-\overset{\overset{H}{|}}{N}-CH_3} + HONO \longrightarrow \underset{N\text{-Nitroso-}N\text{-methyl aniline}}{Ph-N(CH_3)-N{=}O} + H_2O$$

7.10.4 3° Amines

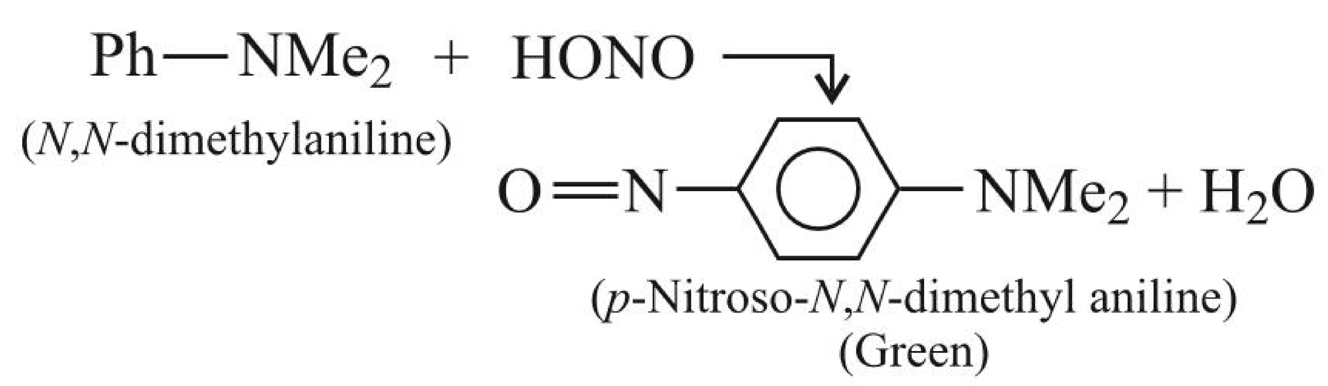
Aliphatic 3° amines on reaction with HONO form soluble nitrite salts, while aromatic 3° amines undergo SE reaction in the ring to form green-coloured *p*-nitroso amines.

7.10.5 3° Aliphatic Amine

$$\underset{(R{=}CH_3)}{R_3N} + HONO \longrightarrow \underset{\substack{\text{Trialkyl ammonium}\\ \text{nitrite (soluble)}}}{[R_3\overset{\oplus}{N}H]NO_2^{\ominus}} \xrightarrow{\Delta} \underset{\text{Yellow oil}}{CH_3-\overset{\overset{CH_3}{|}}{N}-N{=}O} + CH_3OH$$

(This is called Cope reaction)

7.10.6 3° Aromatic Amine



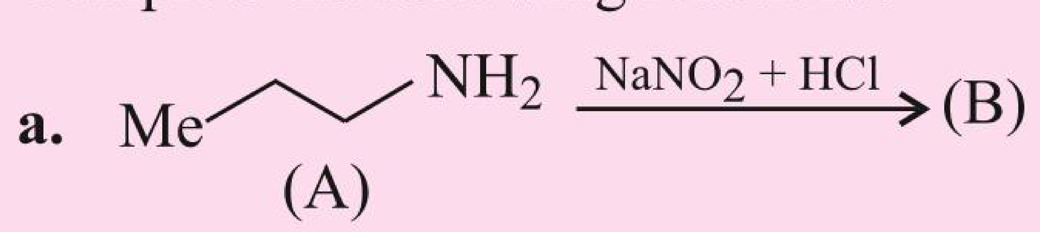
Note:

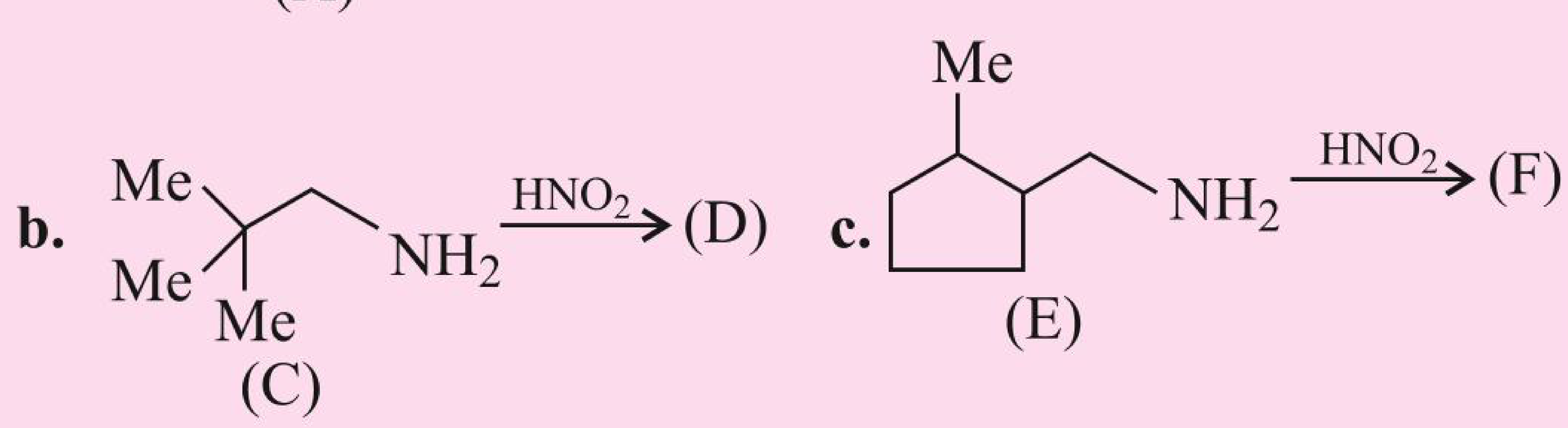
i. HNO_2 is also used to distinguish between 1°, 2°, and 3° nitro compounds. See also Chapter 2, Victor Meyer's method.

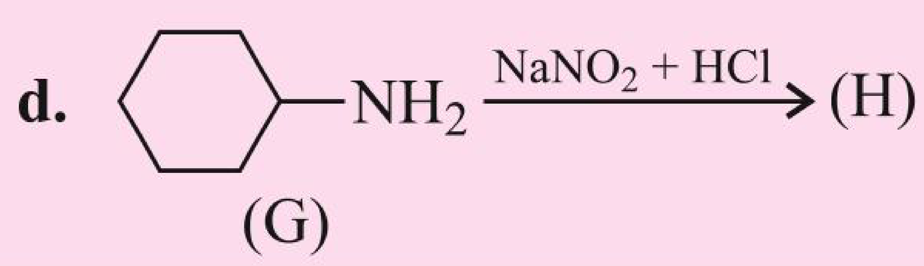
ii. HNO_2 also reacts with aldehydes and ketones. See Chapter 5.

Illustration 7.10

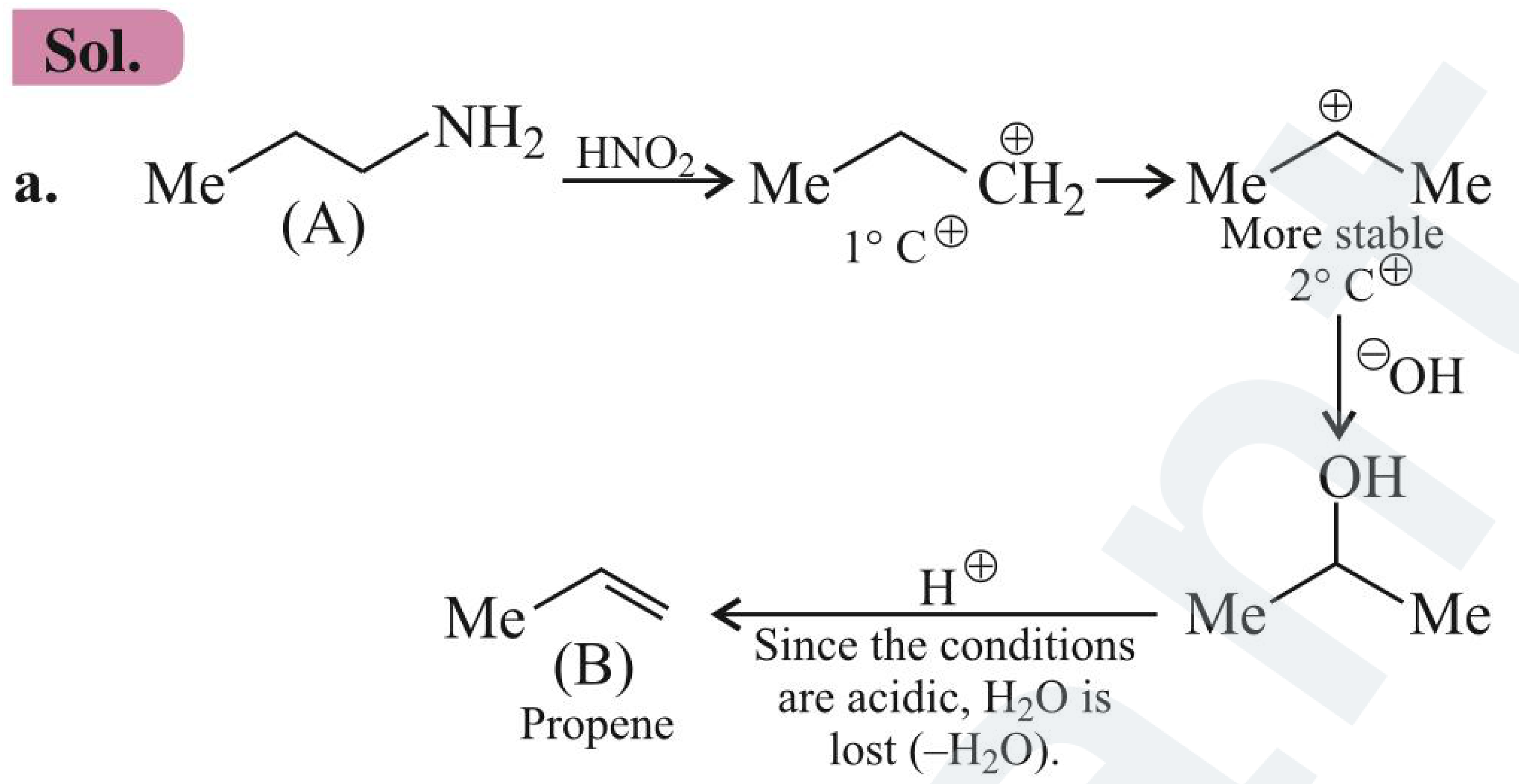
Complete the following reactions:

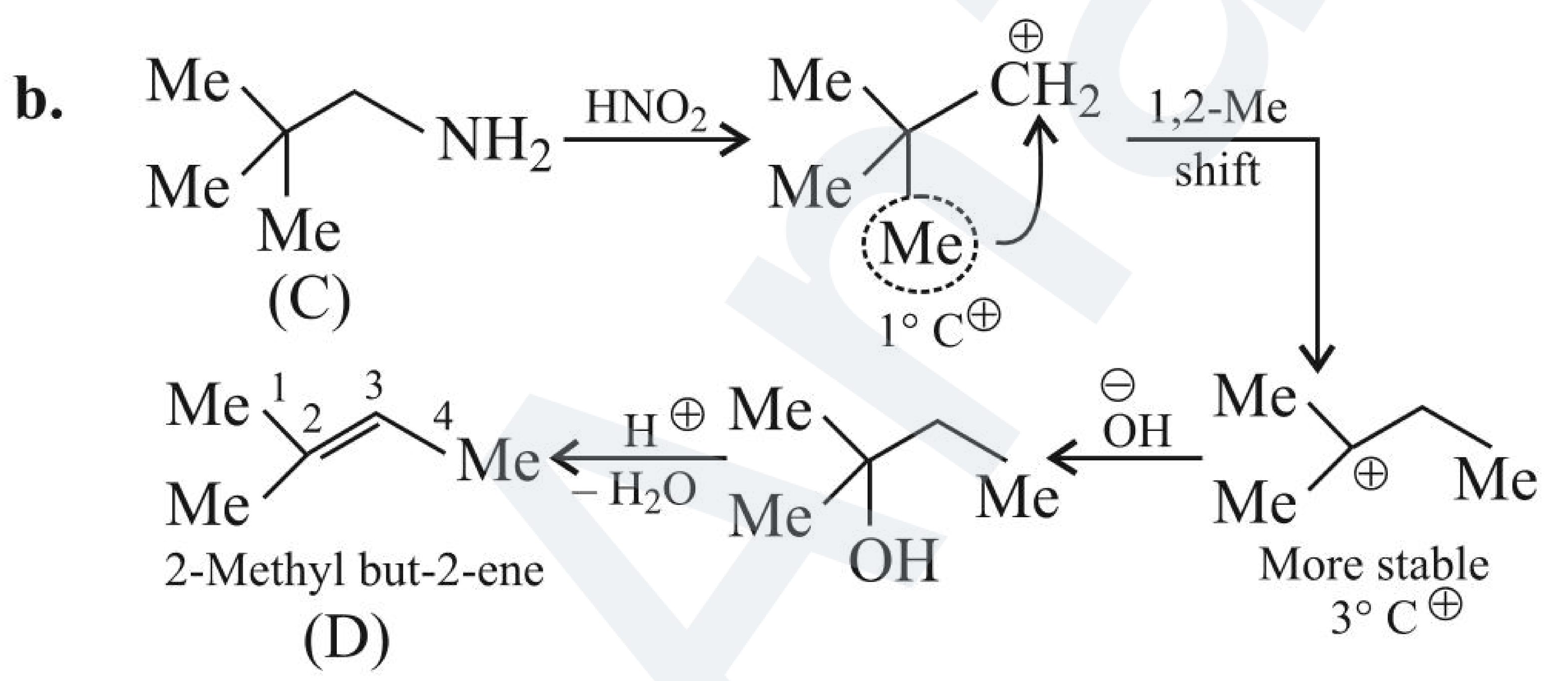


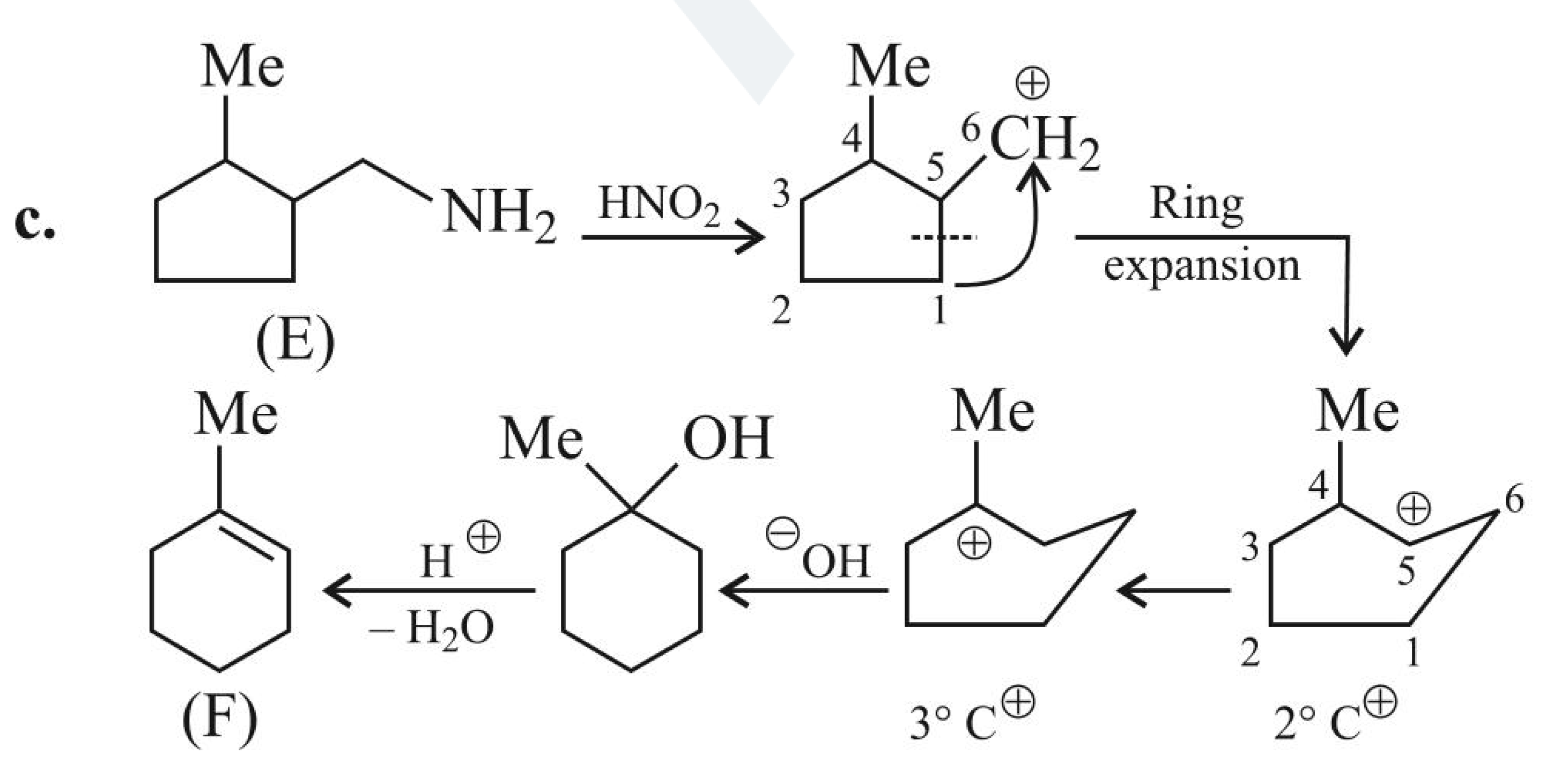


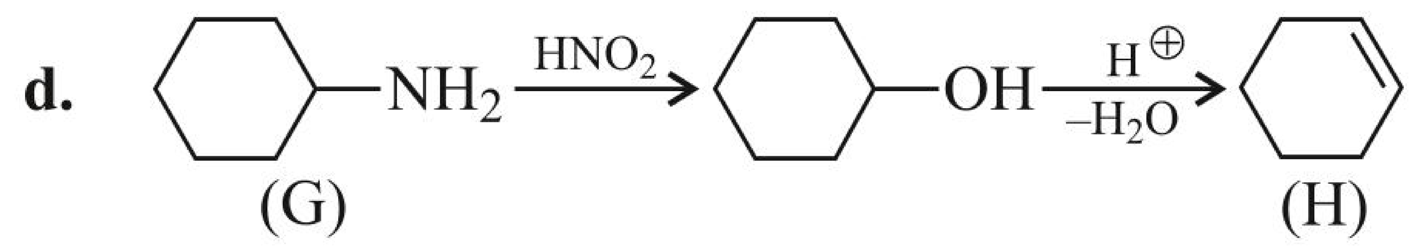


Sol.



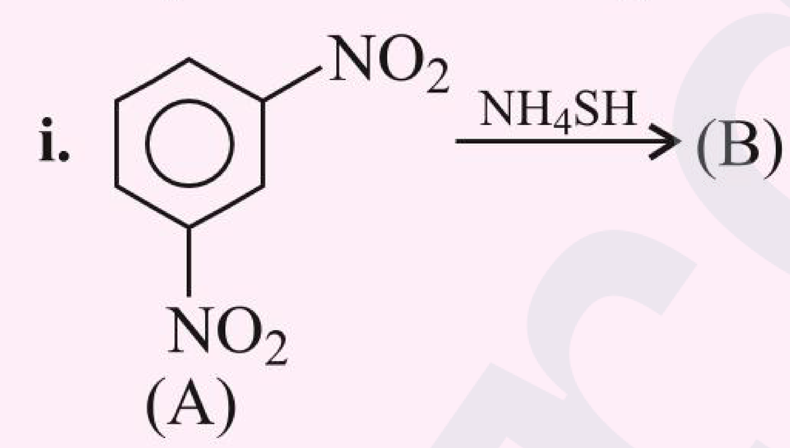


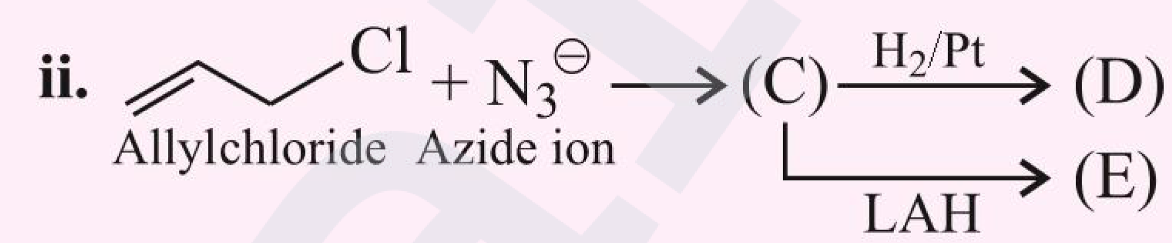




Concept Application Exercise 7.1

1. Complete the following:





2. Complete the following reactions:

a. $PhNO_2 \xrightarrow{Zn + aq.\ NH_4Cl} (I)$

b. $p\text{-}Me—C_6H_4NO_2 \xrightarrow{As_2O_3/Aq.\ NaOH} (II)$

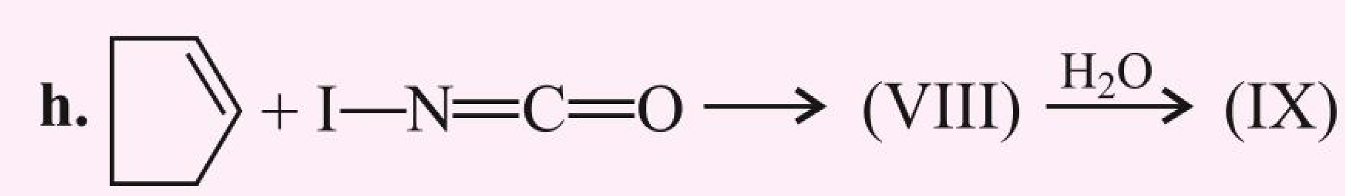
c. $m\text{-}Me—C_6H_4NO_2 \xrightarrow{LAH} (III)$

d. $PhNO_2 \xrightarrow{Zn + Alc.\ NaOH} (IV)$

e. $p\text{-}Me—C_6H_4NO_2 \xrightarrow[\text{Excess Zn/NaOH}]{H_2NNH_2/\text{Raney Ni or}} (V)$

f. $Ph\overset{\oplus}{N_2}Br^{\ominus} \xrightarrow{Na_2SO_3} (VI)$

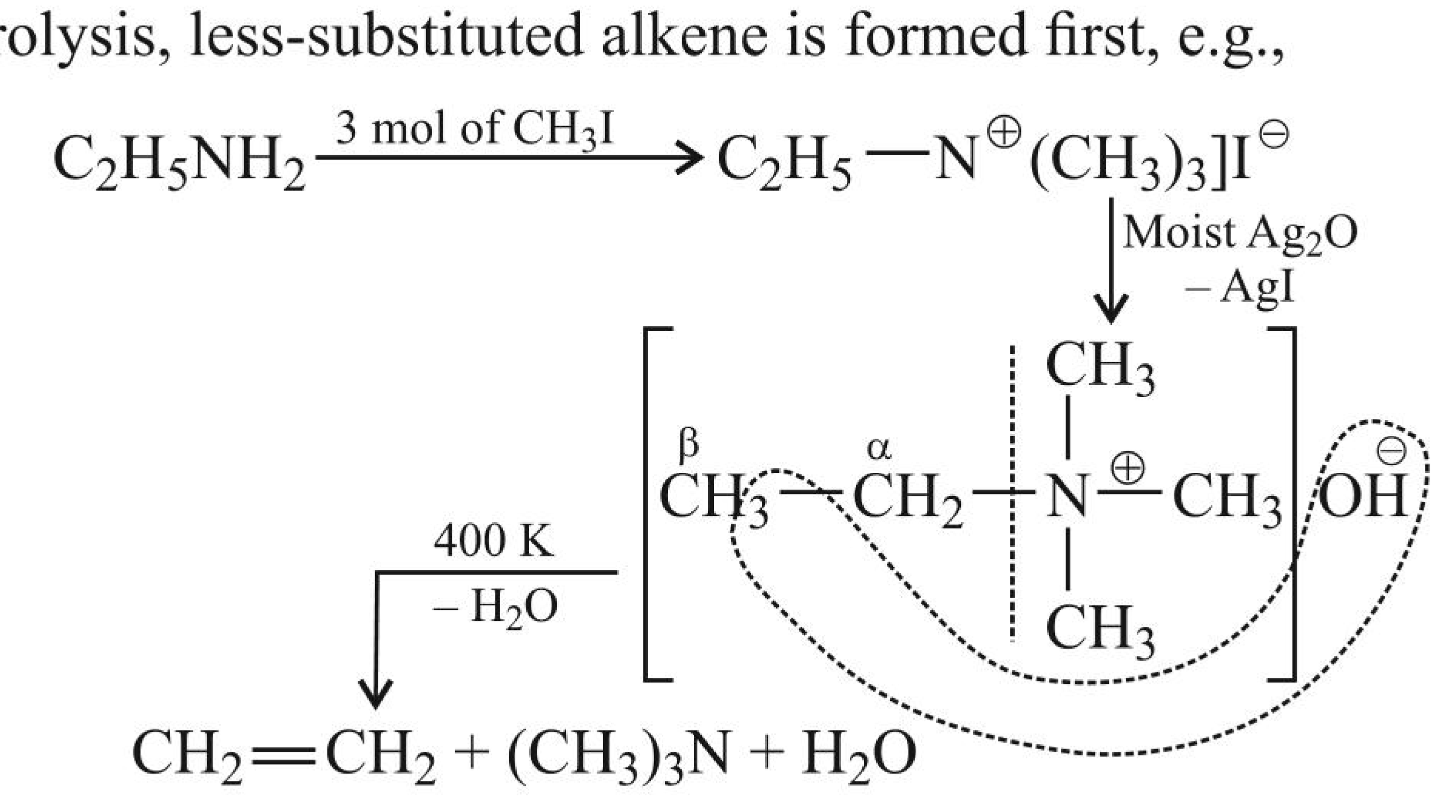
g. $p\text{-}Et—C_6H_4\overset{\oplus}{N_2}Br^{\ominus} \xrightarrow[\text{powder}]{\text{Cu bronze}} (VII)$

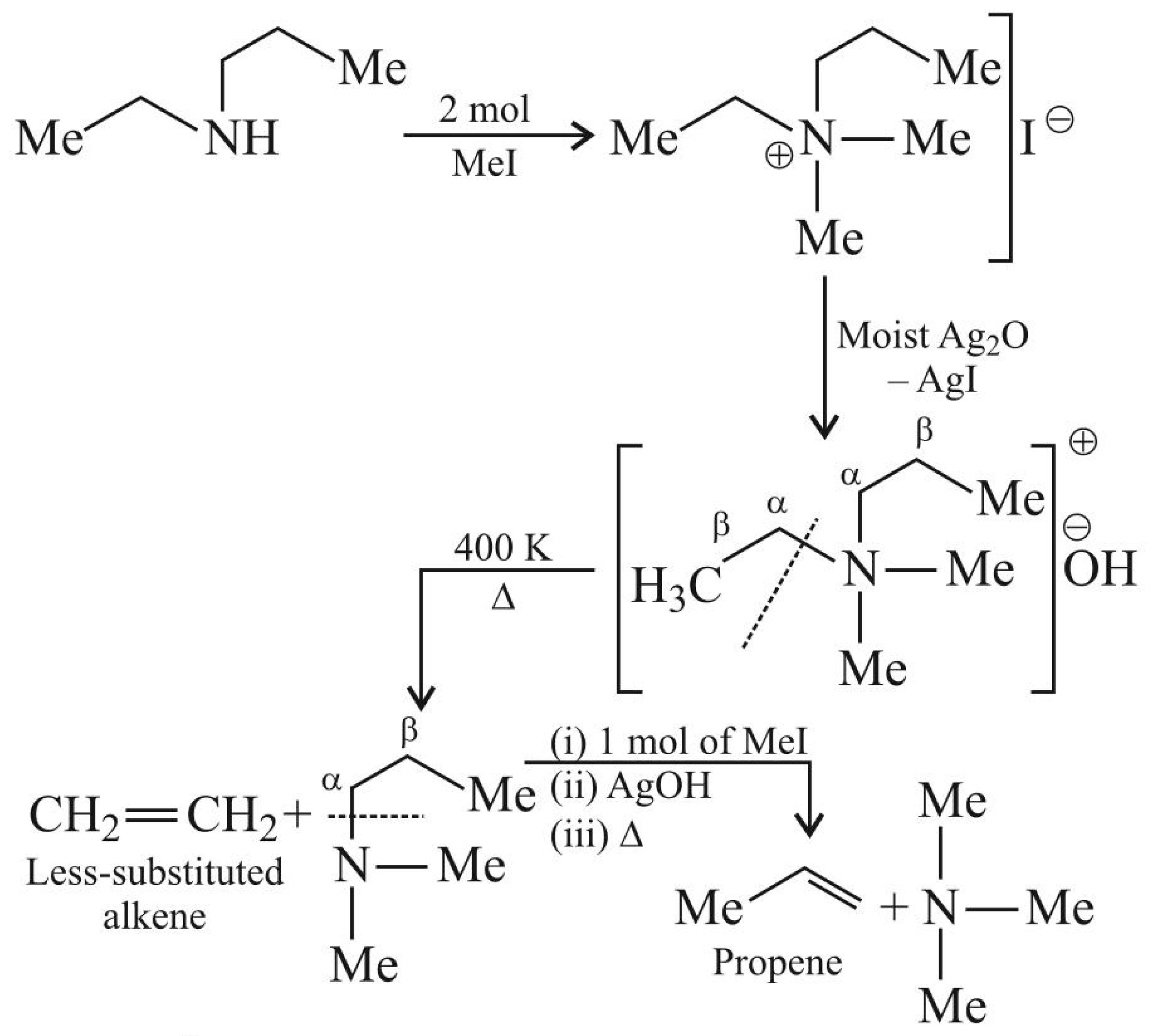


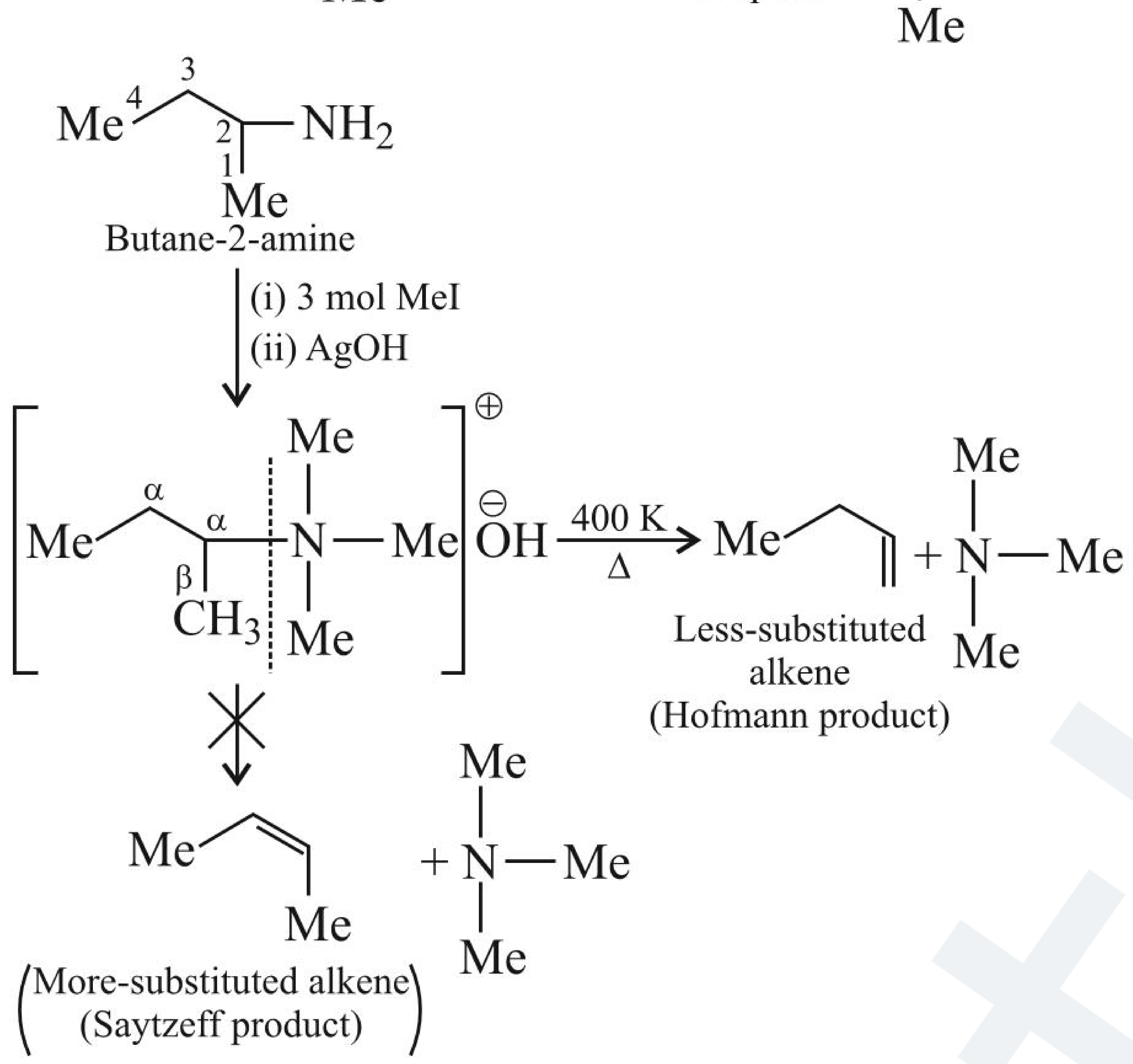
7.11 HOFMANN'S EXHAUSTIVE METHYLATION AND ELIMINATION

The process of converting an amine (1°, 2°, or 3°) into 4° ammonium salt on treatment with excess of CH_3I is called **Hofmann's exhaustive methylation.** This 4° salt when treated with moist Ag_2O gives silver halide as precipitate, and 4° ammonium hydroxide, which on heating at 400 K or above undergoes an elimination reaction to produce an alkene, trimethylamine, and water. This is called **Hofmann's elimination reaction.** In the pyrolysis, less-substituted alkene is formed first, e.g.,

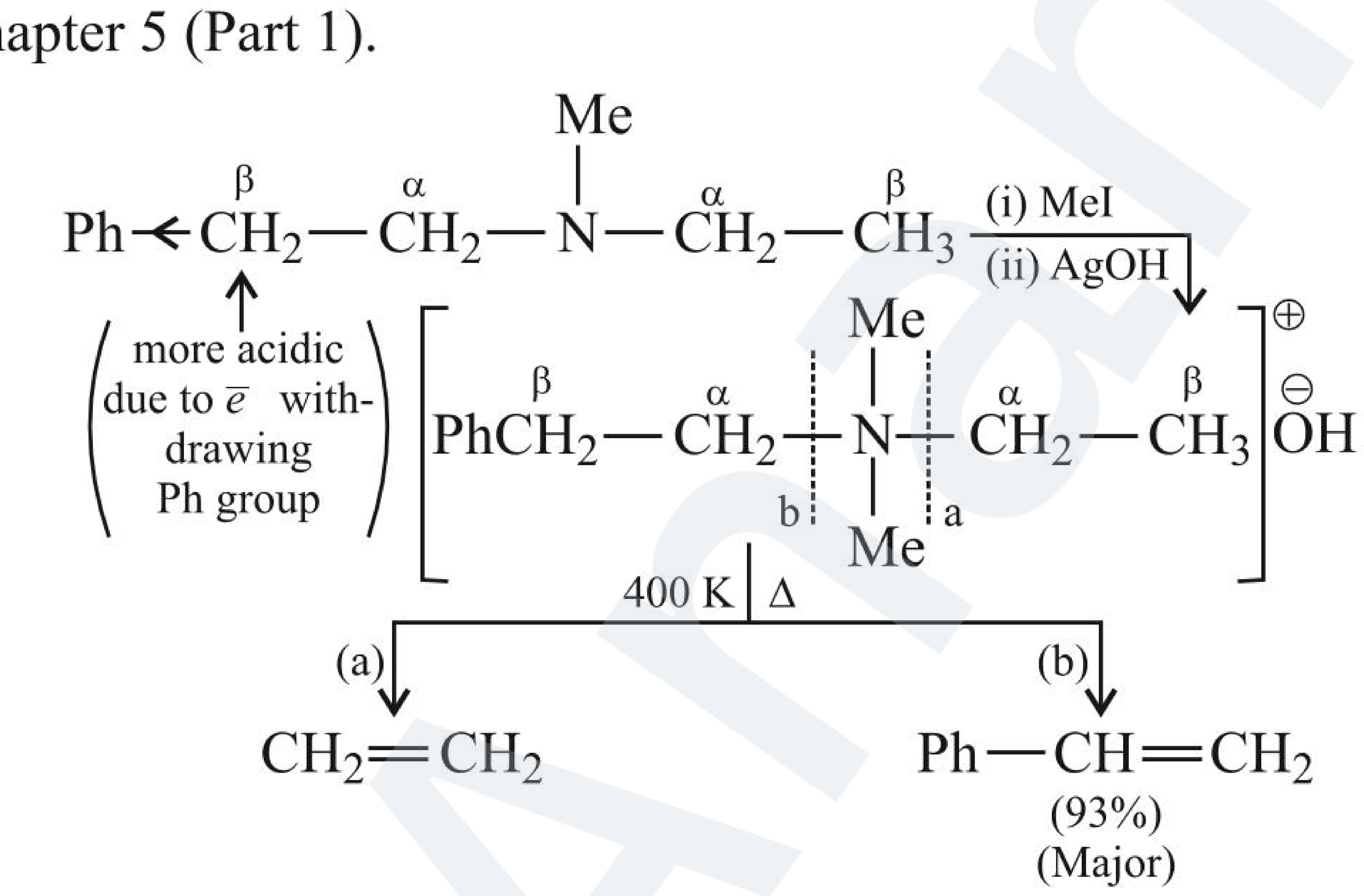
i.



ii. 

iii. 

For explanation on why a less substituted alkene is formed, see Chapter 5 (Part 1).

iv. 

In this case, the alkene formed by path (b) is in major amount because double bond is conjugated with the double bond of (Ph) group.

Note:

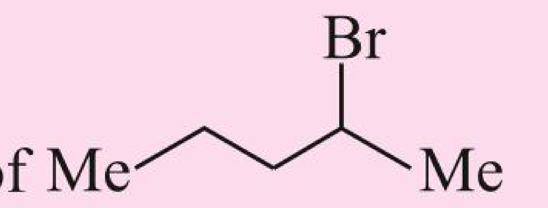
i. This elimination reaction is E2.

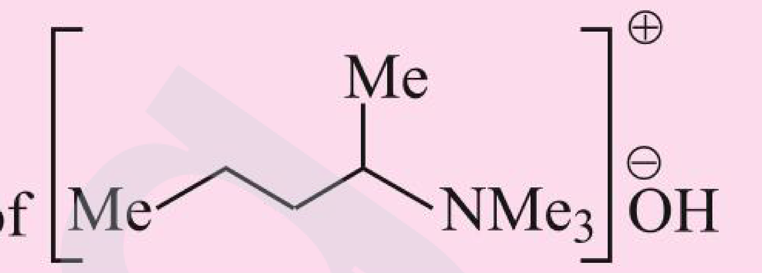
ii. The leaving group in the last step is NMe_3.

iii. $RCH_2CH_2NH_2$ does not undergo an E2 elimination because $\overset{\ominus}{N}H_2$ is a poor leaving group.

ILLUSTRATION 7.11

Explain:

I. Dehydrohalogenation of 

II. Hofmann elimination of 

Sol. **I.** 

II. $\xrightarrow{\Delta}$ 3% (*cis* and *trans*) + (97%)

E2 elimination of an alkyl halide with base ($EtO^{\ominus}$) gives mainly the Saytzeff alkene (i.e., more-substituted alkene), whereas 4° ammonium salt undergoes Hofmann elimination to give less-substituted alkene, resulting from a loss of more acidic β-H (1° > 2° > 3°) called Hofmann's rule. Thus, the acidity of β-H is more important than the stability of the alkene that is formed.

7.12 OXIDATION OF AMINES AND COPE REACTION

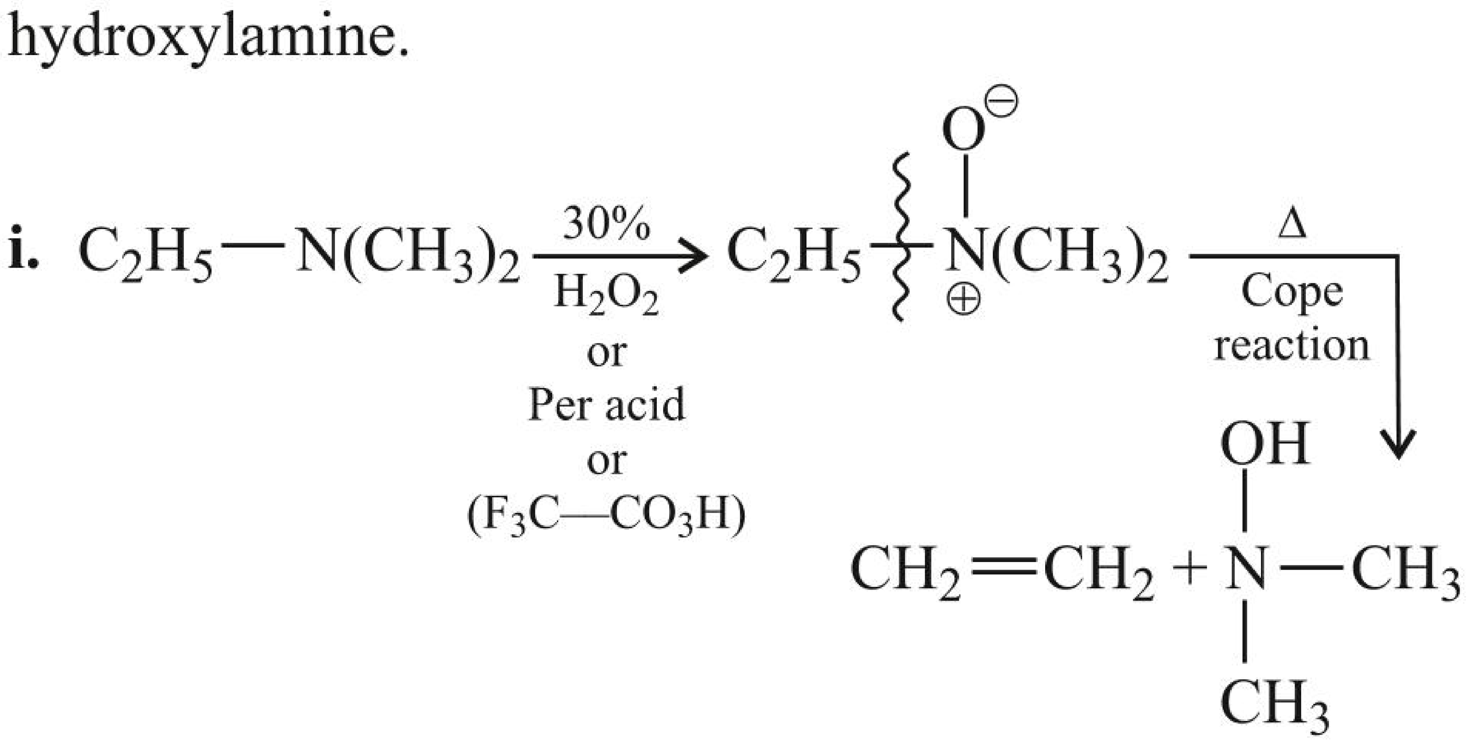
1° amines undergo oxidation to nitro compounds through a sequence of steps given below. Depending upon the reagent, various species such as hydroxylamine, nitroso, and nitro compounds are formed. 1° amine having (—NH_2) group at 3° C atom is oxidised with acidic $KMnO_4$ to a nitro compound in excellent yield. Such a nitro compound cannot be easily prepared in any other way. 3° amines are not oxidised by $KMnO_4$, but Caro's acid (H_2SO_5), or O_3 or H_2O_2 oxidises 3° amine to 3° amine oxide.

i. $RNH_2 \longrightarrow RNHOH \longrightarrow RNO \longrightarrow RNO_2$

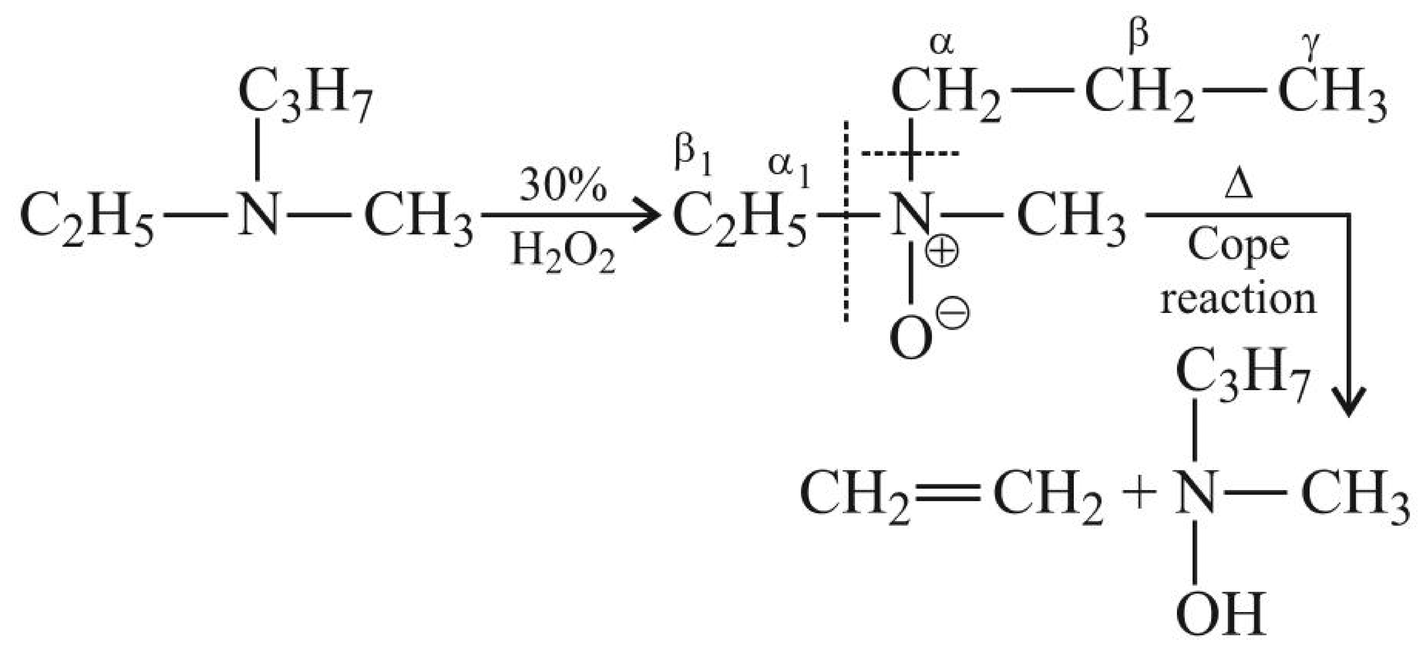
ii. $R_3C{-}NH_2 \xrightarrow{KMnO_4} R_3C{-}NO_2$

7.12.1 Cope Reaction

3° amine oxide on heating gives alkene and N,N-dialkyl hydroxylamine.

i. 

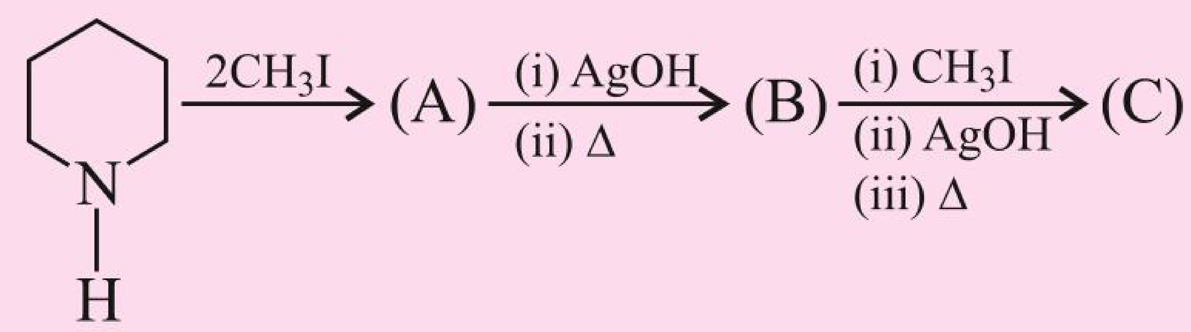
In Cope reaction, the alkene formed will be less substituted (not Saytzeff product but Hofmann elimination product). Cope reaction is similar to Hofmann exhaustive methylation and elimination reaction.

ii. 

iii. Cope reaction is an E2 reaction in which leaving groups are H and $R_2N—O^{\ominus}$, which form $R_3N—OH$.

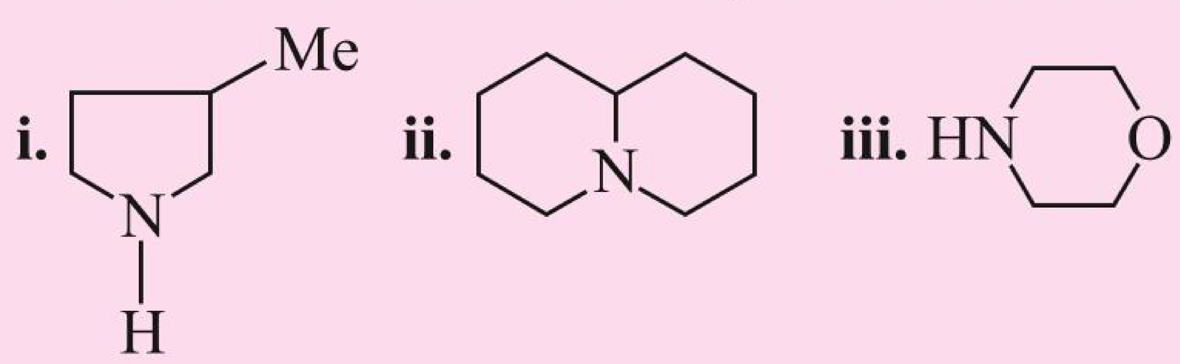
ILLUSTRATION 7.12

Complete the following:

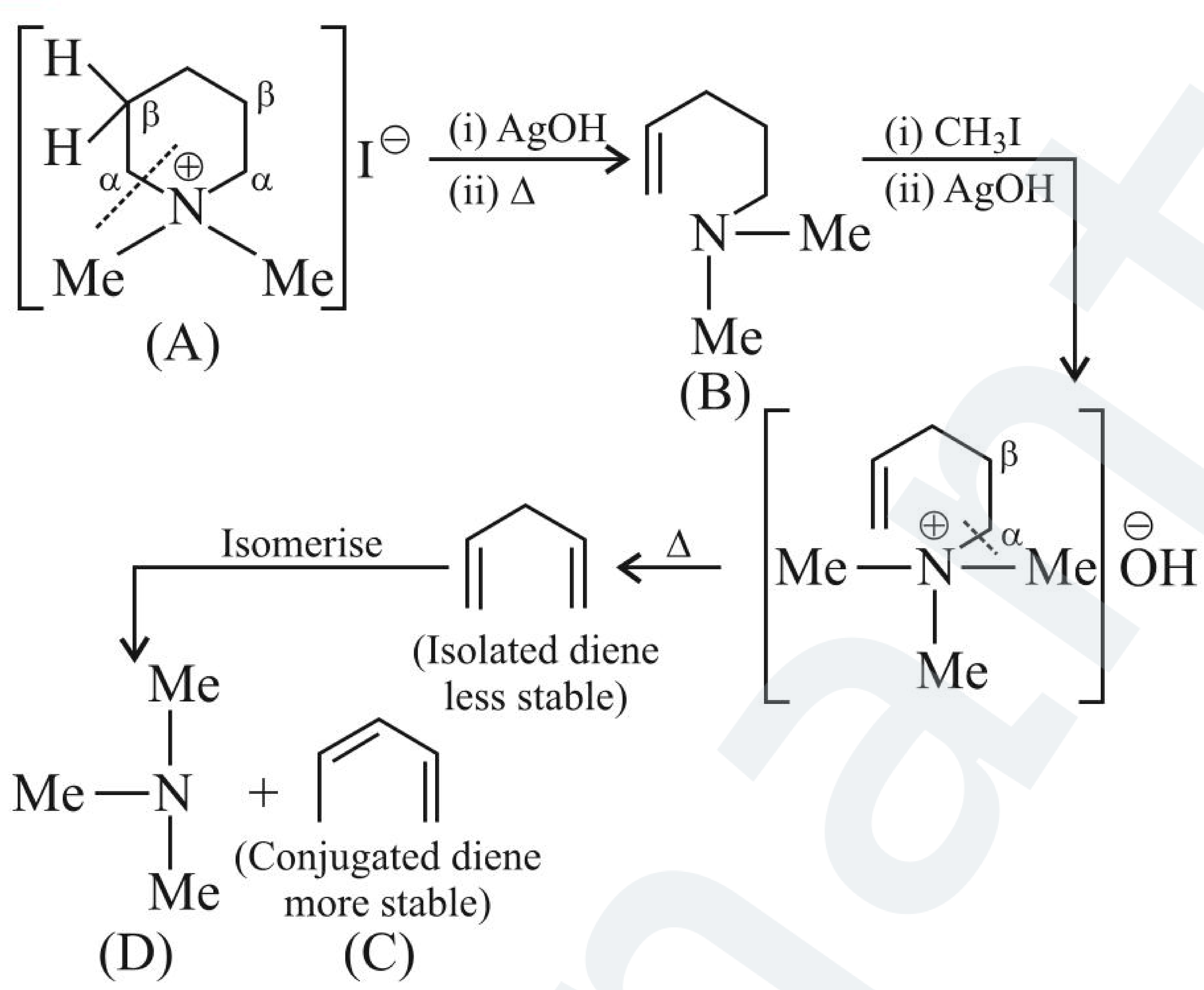
a. 

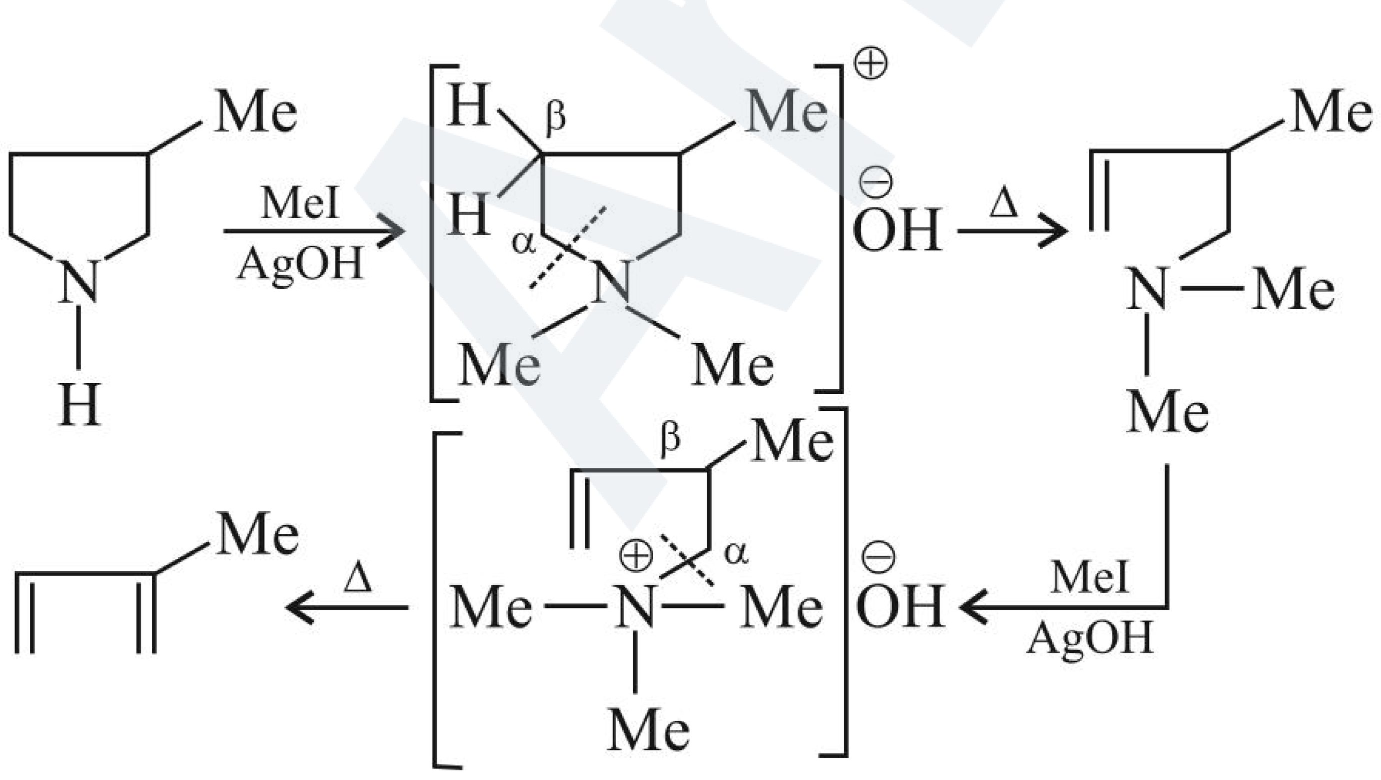
Piperidine

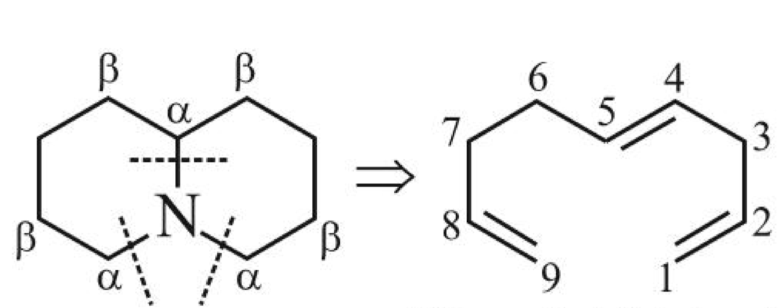
b. Give the products of the following by application of Hofmann's exhaustive methylation and elimination:



Sol.

a. 

b. i. 

ii. Direct answer: 

(Nona-1,4,8-triene)

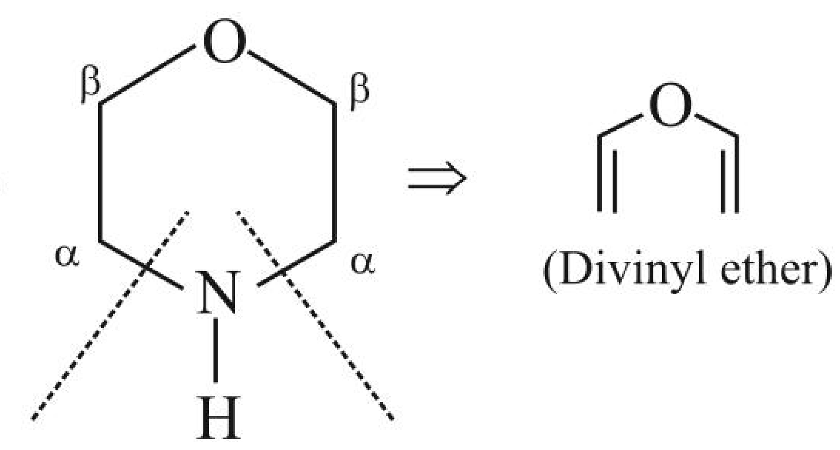
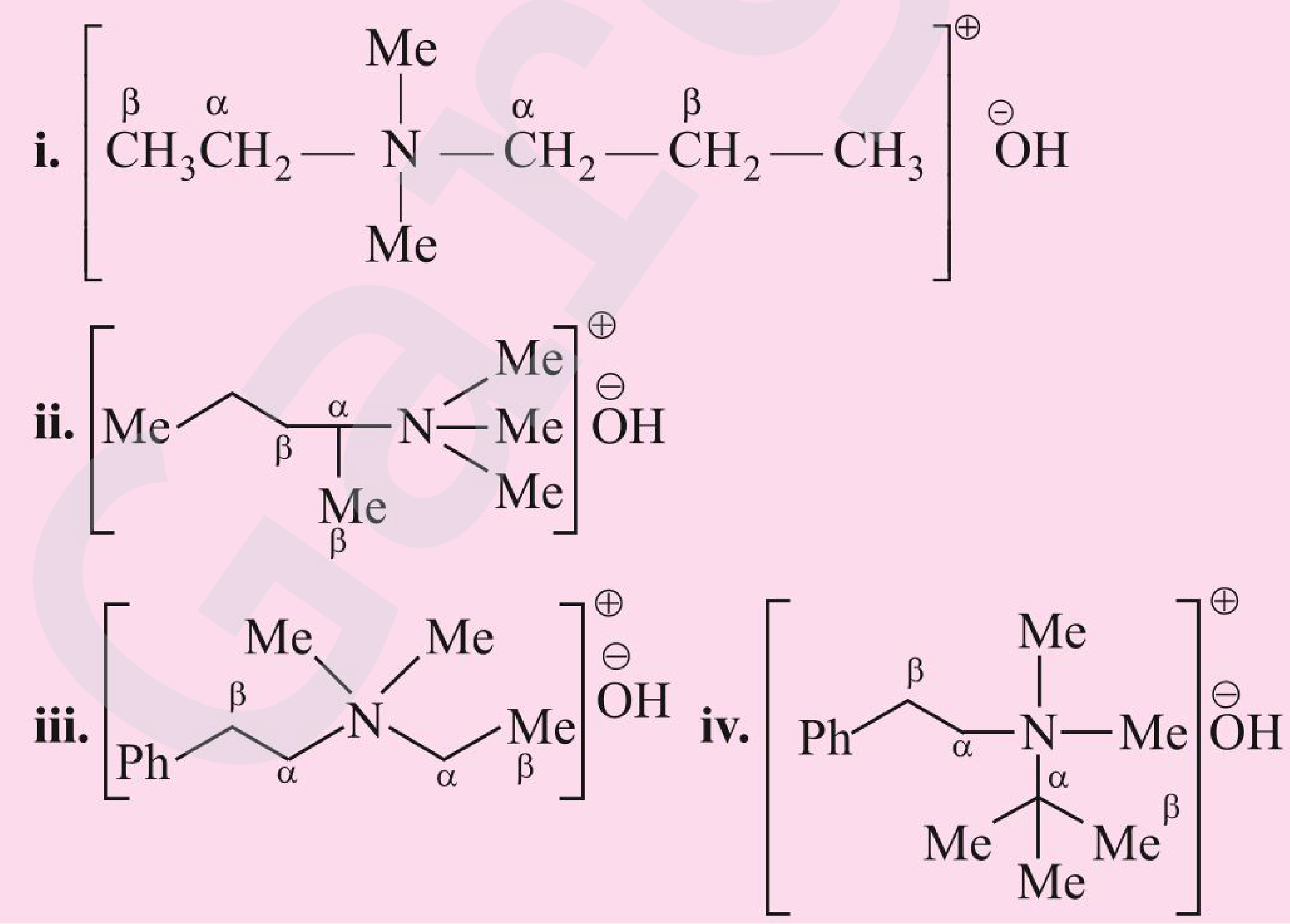
iii. 

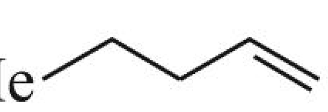
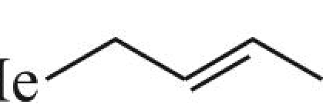
ILLUSTRATION 7.13

Give the alkene formed on heating the following (Hofmann degradation):



Sol.

i. Less-substituted alkene $CH_2{=}CH_2$ is formed, not $CH_2{=}CH—CH_3$.

ii. Me is formed, not MeMe.

iii. Here, Saytzeff product is formed not Hofmann product because benzylic H atom's acidic character is greatly increased and the stability of the conjugated alkene influences the reaction.

PH—CH=CH_2 is formed; not $CH_2{=}CH_2$.

iv. PH—CH=CH_2 is formed, not $(Me)_2C{=}CH_2$ [same explanation as in (iii) above].

7.13 TEST FOR AMINES

7.13.1 Solubility Test

1°, 2°, 3° amines, being basic, dissolve in acids such as HCl, H_2SO_4, and HNO_3 and form salts, e.g., $R\overset{\oplus}{N}H_3Cl^{\ominus}$, $[R_2\overset{\oplus}{N}H_3]_2\,SO_4^{2-}$ (Dialkyl ammonium sulphate), $R_3\overset{\oplus}{N}HNO_3^{\ominus}$ (Trialkyl ammonium nitrate). Amines also react with chloroplatinic acid (H_2PtCl_6) to form insoluble salts called chloroplatinates.

$$[2RNH_2 + H_2PtCl_6 \longrightarrow (R\overset{\oplus}{N}H_3)_2PtCl_6^{2-}]$$

7.13.2 Reaction with Metal Ions

Like NH_3, amines also form soluble coordination compounds with transition metal ions such as Ag^+, Cu^{2+} ions, etc. Thus, AgCl dissolves in methylamine solution due to the formation of soluble complex salt, e.g.,

i. $AgCl + 2CH_3NH_2 \longrightarrow$

$$[CH_3\overset{H}{\underset{H}{N}}{:} \rightarrow Ag \leftarrow {:}NH_2CH_3]^{\oplus}Cl^{\ominus}$$

or

$$[Ag(CH_3\dot{N}H_2)_2]^{\oplus}Cl^{\ominus}$$

$$AgCl + 2NH_3 \longrightarrow [Ag(NH_3)_2]^{\oplus}Cl^{\ominus}$$

ii. Similarly like NH_3, amines react with Cu^{2+} ions to form deep-blue solution, due to the formation of soluble complex salt, e.g.,

$$CuCl_2 + 4CH_3NH_2 \longrightarrow [Cu(CH_3NH_2)_4]^{2+}\ (Cl^-)_2$$

$$CuCl_2 + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{2+}\ (Cl^-)_2$$

7.13.3 Hinsberg's Test

Reaction with aryl sulphonyl chloride (to distinguish between 1°, 2°, and 3° amines):

i. $$\underset{\text{Benzene sulphonyl chloride (Hinsberg's reagent)}}{Ph{-}SO_2Cl} + \underset{1^\circ\text{ amine}}{H{-}NH{-}R} \xrightarrow{-HCl} \underset{N\text{-Alkyl benzene sulphonamide}}{\left[Ph{-}SO_2{-}\underset{R}{NH}\right]}$$

$$\xrightarrow[-H_2O]{KOH} \underset{\text{Pot. salt soluble in KOH}}{\left[PhSO_2\overset{\ominus}{\underset{R}{N}}{-}K^{\oplus}\right]} \xrightarrow[HCl]{-KCl} \underset{N\text{-Alkyl benzene-sulphonamide (Insoluble in HCl)}}{PhSO_2NHR}$$

ii. $$PhSO_2Cl + \underset{2^\circ\text{ amine}}{H{-}NR_2} \xrightarrow{KOH} \underset{N,N\text{-Dialkyl benzene sulphonamide (insoluble in water)}}{PhSO_2NR_2} + HCl$$

iii. $$PhSO_2Cl + \underset{3^\circ\text{ amine}}{NR_3} \longrightarrow \underset{(3^\circ\text{ amine remains insoluble in KOH})}{\text{No reaction}} \xrightarrow{HCl} \underset{\text{(Trialkyl ammonium chloride (Soluble in HCl)}}{R_3\overset{\oplus}{N}HCl^{\ominus}}$$

Separation: The mixture of amines is treated with Hinsberg's reagent (H.R.) followed by the addition of alkali and ether. 1° amines form sulphonamides which dissolve in alkali forming salt and form the aqueous layer. 2° amines form sulphonamides which are soluble in ether and form the upper layer. 3° amines do not react with H.R. and are also soluble in ether. The two layers are separated and 3° amines are obtained by fractional distillation of the ethereal layer. The residue is treated with concentration HCl followed by NaOH, whereupon 2° amine is obtained, e.g.,

$$PhSO_2NR_2 + HCl + H_2O \rightarrow PhSO_3H + R_2NH.HCl \xrightarrow{NaOH} H_2O + NaCl + R_2NH$$

The aqueous layer is acidified with dil. HCl and then hydrolysed with conc. HCl to yield hydrochloride which is then distilled over NaOH, and 1°amine is obtained.

$$PhSO_2.NHR + HCl + H_2O \rightarrow PhSO_3H + R\overset{\oplus}{N}H_3.Cl^{\ominus} \xrightarrow{NaOH} H_2O + NaCl + RNH_2$$

Note: Amines must be water insoluble liquids.

7.13.4 Reaction with *p*-Tolyl Sulphonyl Chloride

Nowadays, a better reagent than Hinsberg reagent, i.e., *p*-tolyl sulphonyl chloride (p-$CH_3{-}C_6H_4{-}SO_2Cl$), is used. The advantage of this reagent over H.R. is that 1° and 2° amines give solid product which can easily be separated by crystallisation.

7.13.5 Hofmann's Method

(Diethyl oxalate is used)

$$\underset{\text{Diethyl oxalate}}{\begin{matrix}COOEt\\ |\\ COOEt\end{matrix}} + 2H_2NR \longrightarrow \underset{\text{Oxamide (solid)}}{\begin{matrix}CONHR\\ |\\ CONHR\end{matrix}} + EtOH$$

$$\begin{matrix}COOEt\\ |\\ COOEt\end{matrix} + 2HNR_2 \longrightarrow \underset{\text{Oxamic ester (liquid)}}{\begin{matrix}CONR_2\\ |\\ COOEt\end{matrix}} + EtOH$$

3° amine does not react.

Separation: The solid oxamide is separated and heated with KOH when 1° amine is obtained. The liquid (mixture of oxamic ester + 3° amine) is subjected to fractional distillation. Oxamic ester is again decomposed by heating with KOH to get 2° amine, e.g.,

$$\begin{matrix}COHNR\\ |\\ COHNR\end{matrix} + 2KOH \longrightarrow \underset{\text{Pot. oxalate}}{\begin{matrix}COOK\\ |\\ COOK\end{matrix}} + \underset{1^\circ\text{ amine}}{2RNH_2}$$

$$\begin{matrix}CONR_2\\ |\\ COOEt\end{matrix} + 2KOH \longrightarrow \begin{matrix}COOK\\ |\\ COOK\end{matrix} + \underset{2^\circ\text{ amine}}{2R_2NH} + EtOH$$

Fractional distillation: The mixture of amines is subjected to fractional distillation and separated into constituents.

7.14 ELECTROPHILIC SUBSTITUTION (SE) REACTIONS

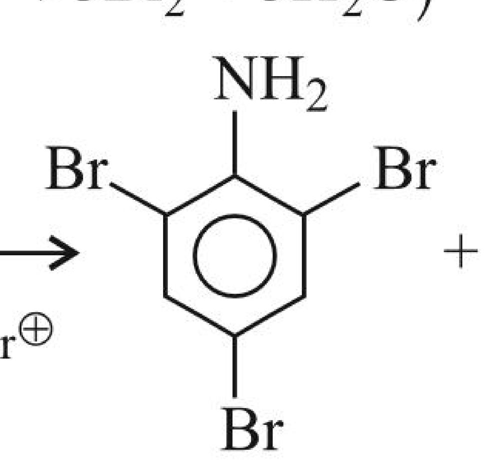
Aniline is a resonance hybrid of five structures, due to which $\bar{e}$ density at *o*- and *p*-positions is highest, so ($-NH_2$) group is *o*- and *p*-directing and a powerful activating group.

7.14.1 Bromination

Aniline reacts with Br_2 water at room temperature or with brominating reagent to give a white precipitate of 2,4,6-tribromo aniline.

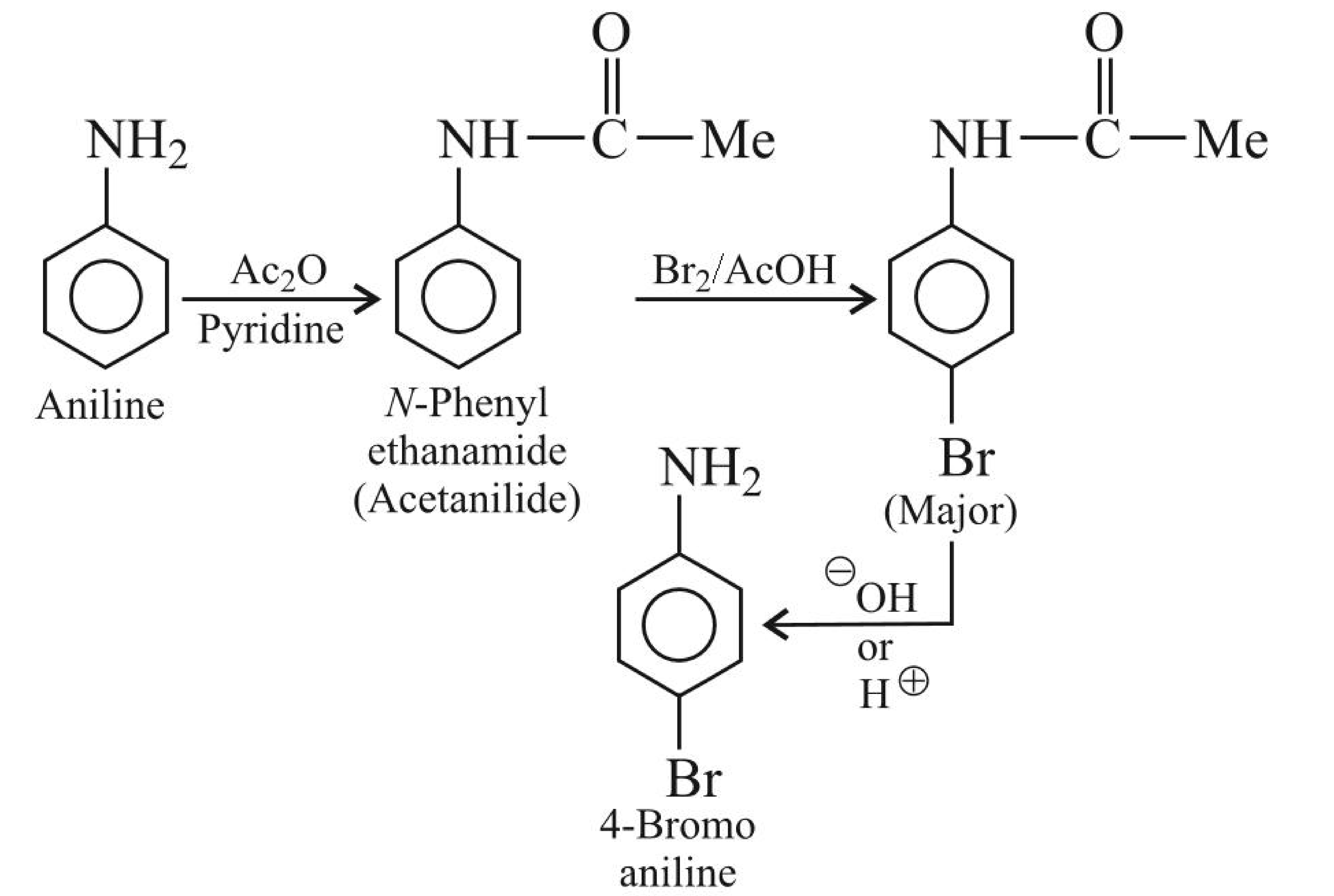
$$\left(BrO_3^{\ominus} + 5Br^{\ominus} + 6H^{\oplus} \rightarrow 3Br_2 + 3H_2O\right)$$

$$PhNH_2 + 3Br_2 \xrightarrow[\text{or } BrO_3^{\ominus} + 5Br^{\oplus} + 6H]{Br_2/H_2O}$$

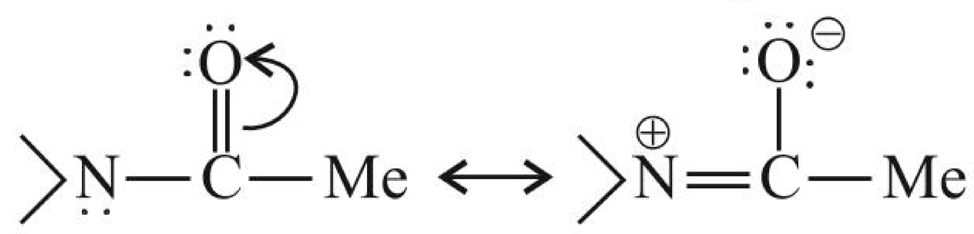


$+ 3HBr$

Since aromatic amines are of very high reactivity, so to prepare mono-substituted aniline derivative, ($-NH_2$) group is protected by acetylation with acetic anhydride (Ac_2O), then the desired substitution is carried out followed by hydrolysis the of the substituted amide to the substituted amine.

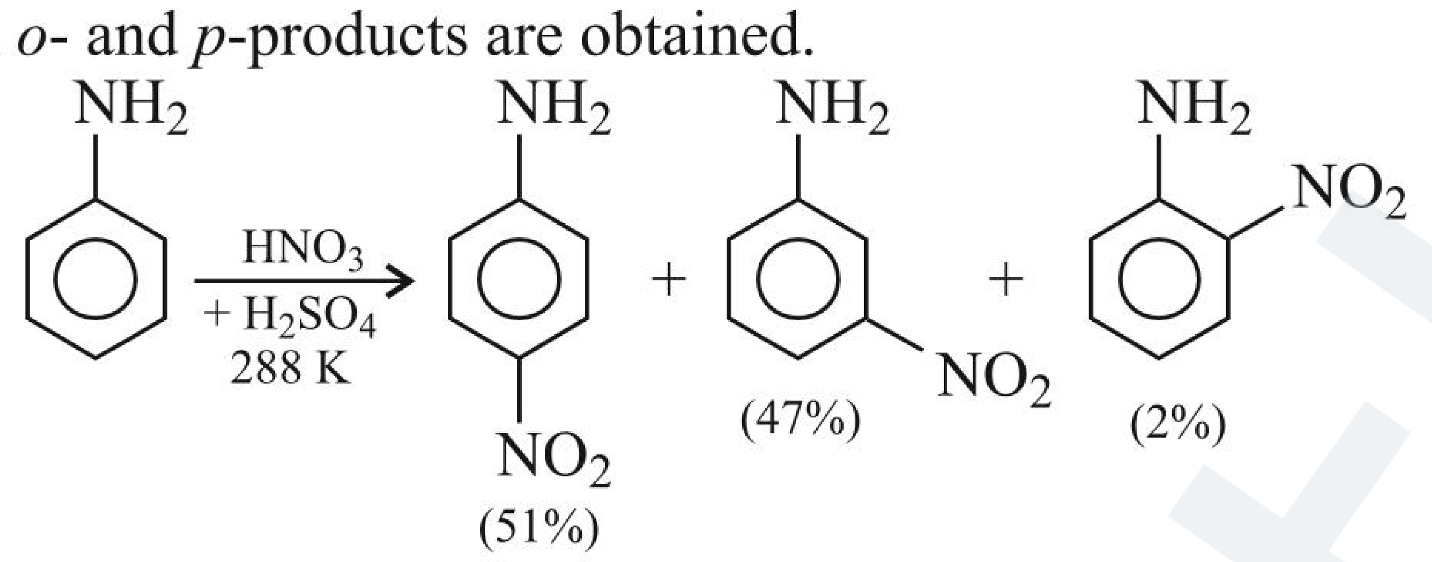


The LP $\bar{e}$'s on N atom of acetanilide interact with O atom due to resonance (i.e., cross conjugation). Hence, LP $\bar{e}$'s on N atom are less available for donation to benzene ring by resonance, thereby decreasing the activating effect of (—NH_2) group.

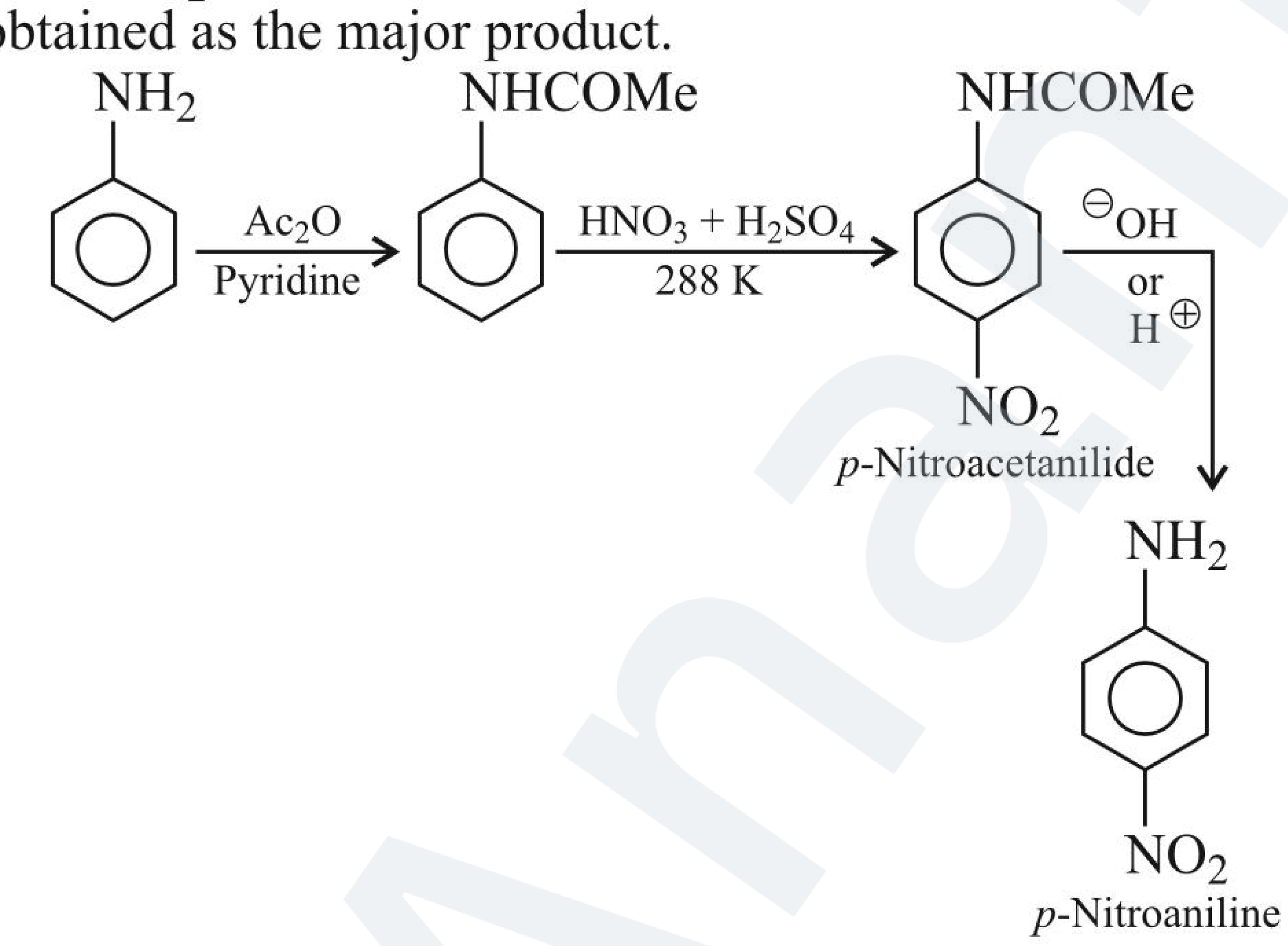


7.14.2 Nitration

The direct nitration of aniline gives tarry oxidation products along with nitro derivatives. In the acidic medium, aniline is protonated to give anilinium ion which is *m*-directing, so *m*-derivative along with *o*- and *p*-products are obtained.

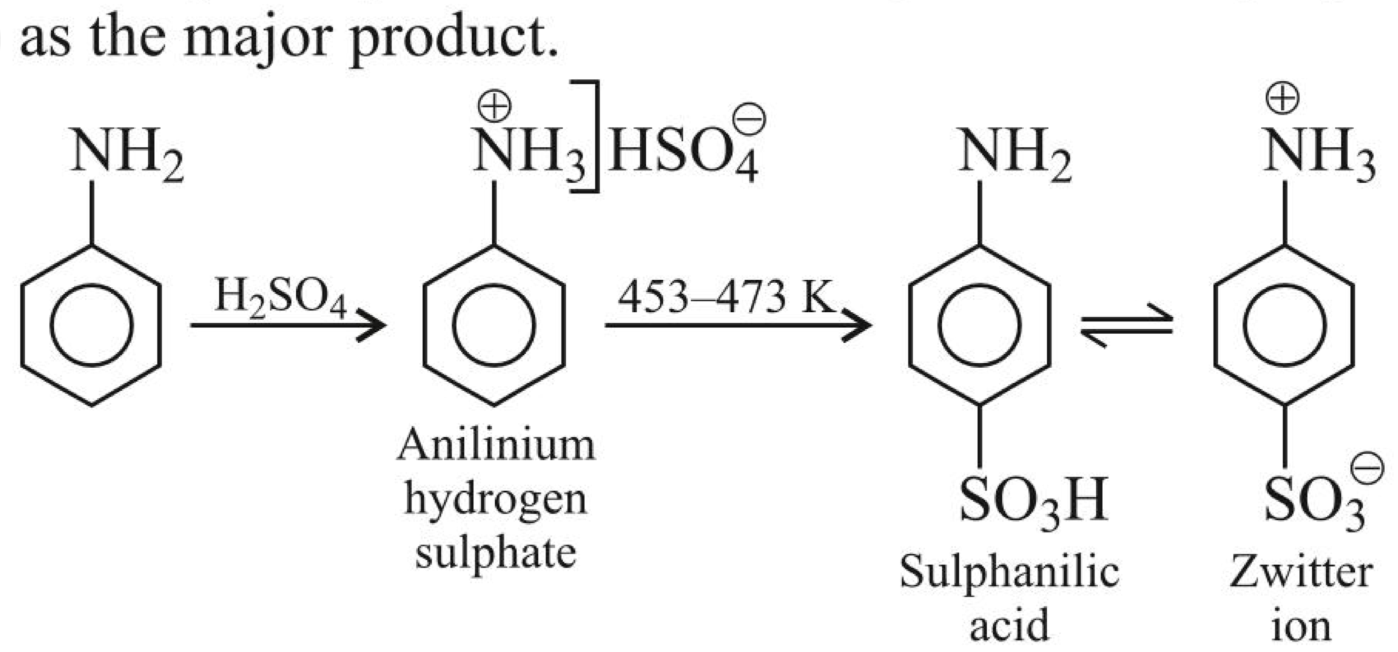


If (—NH_2) group is protected by acetylation, *p*-nitro derivative is obtained as the major product.



7.14.3 Sulphonation

Aniline on sulphonation with concentrated H_2SO_4 first gives anilium hydrogen sulphate, which on heating with H_2SO_4 at 453–473 K yields *p*-aminobenzene sulphonic acid (sulphanilic acid) as the major product.



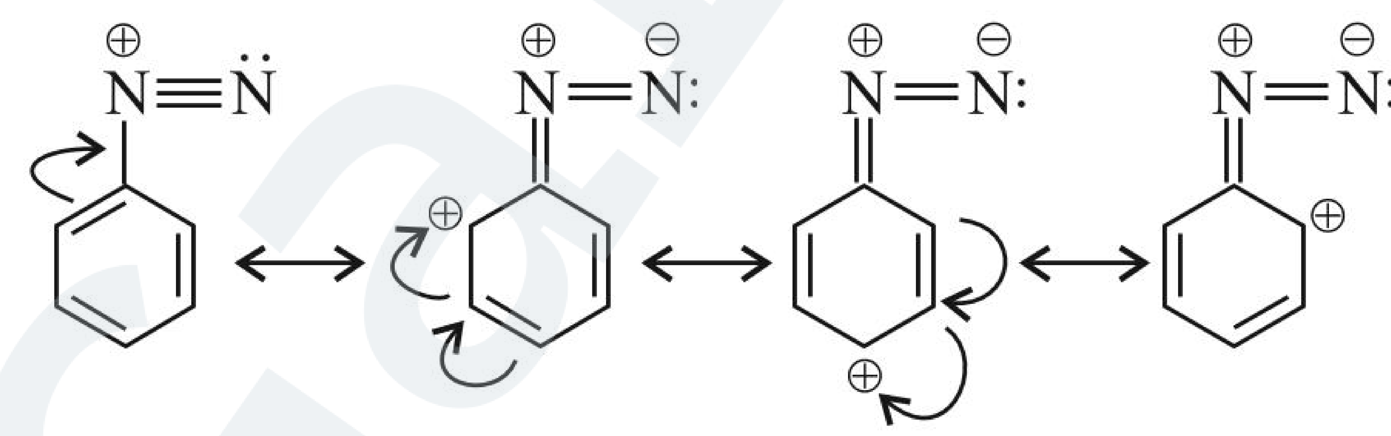
7.14.4 Friedel–Crafts Reaction

Aniline does not undergo F.C. reaction (both alkylation and acetylation) due to salt formation with $AlCl_3$, the Lewis acid which acts as a catalyst. Due to this, N atom of aniline acquires positive charge and hence acts as a strong deactivating group for further reaction.

7.15 DIAZONIUM SALTS

7.15.1 Introduction

1° aromatic amines form arene diazonium salts which are stable for a short time in solution at low temperature unlike 1° aliphatic amines which form highly unstable alkyl diazonium salts. The stability of arenediazonium ion is due to resonance stabilisation.



7.15.2 Diazotisation

The conversion of 1° aromatic amine into diazonium salt with HNO_2 (nitrous acid) is known as diazotisation. HNO_2 is produced in the reaction mixture by the reaction of $NaNO_2$ and HCl. Due to instability, diazonium salts are used immediately after their preparation.

$$\text{PhNH}_2 + \text{NaNO}_2 + \text{HCl} \xrightarrow{273\text{–}278\text{ K}} \underset{\text{Benzene diazonium chloride (I)}}{[\text{Ph—}\overset{\oplus}{\text{N}}\equiv\text{N}]\text{Cl}^{\ominus}} + \text{NaCl} + 2\text{H}_2\text{O}$$

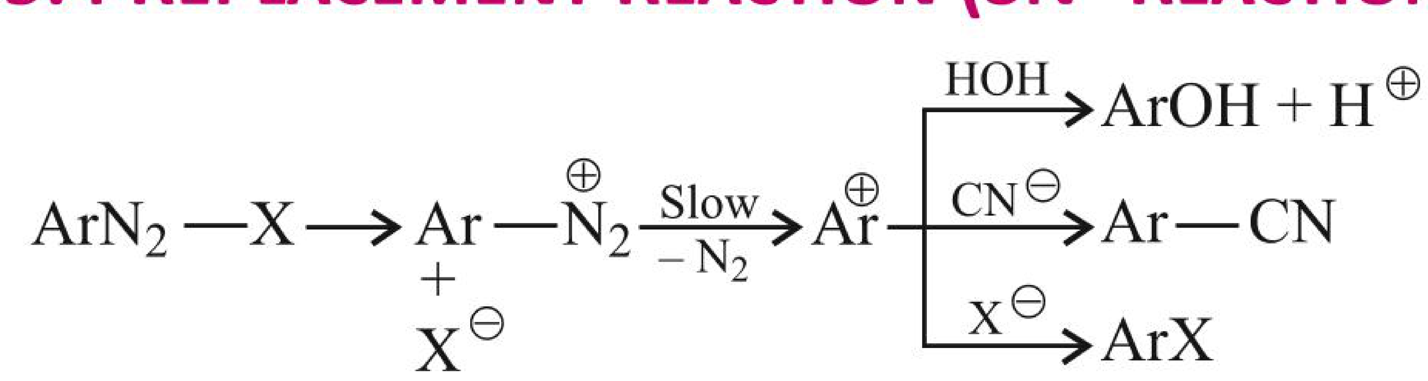
(I) is a colourless crystalline solid, readily soluble in H_2O, and is stable in cold but reacts with H_2O when heated. It decomposes easily in the dry state. Benzene diazonium fluoroborate $[\text{Ph—N}^{\oplus}\equiv\text{N})\text{BF}_4^{\ominus}]$ is water insoluble and stable at room temperature.

The reactions of diazonium salts are broadly of two types: (a) reactions involving displacement of nitrogen and (b) reactions involving retention of diazo group, called coupling reactions.

7.15.3 Reaction Involving Displacement of Nitrogen

Due to better leaving ability of diazonium group, it is substituted by other groups such as $Cl^{\ominus}$, $Br^{\ominus}$, $I^{\ominus}$, $CN^{\ominus}$, and $\overset{\ominus}{O}H$, which displaces nitrogen from the aromatic ring. The nitrogen formed escapes from the reaction mixture as a gas.

7.15.4 Replacement Reaction (SN[1] Reaction)



7.15.5 Replacement by (OH) Group

$$\text{ArN}_2\text{Cl} + \text{HOH} \xrightarrow{\text{Boiling}} \text{ArOH} + \text{N}_2 + \text{HCl}$$

7.15.6 Replacement by H

On reduction with sodium stannite (Na_2SnO_2) (alkaline $SnCl_2$) or hypophosphorous acid (H_3PO_2) or on warming with C_2H_5OH, ArN_2Cl gives benzene.

$$ArN_2Cl + H_3PO_2 + H_2O \longrightarrow ArH + N_2 + H_3PO_3 + HCl$$

$$ArN_2Cl + Na_2SnO_2 + H_2O \longrightarrow ArH + N_2 + Na_2SnO_3 + HCl$$

7.15.7 Sandmeyer Reaction (Replacement by Halogen)

$$ArN_2Cl + Cu_2Cl_2 + HCl \longrightarrow ArCl + N_2 + 2CuCl_2$$

$$ArN_2Br + Cu_2Br_2 + HBr \longrightarrow ArBr + N_2 + 2CuBr_2$$

7.15.8 Gattermann Reaction

$$ArN_2Cl \xrightarrow{\text{Finely divided Cu/HCl}} ArCl + N_2$$

$$ArN_2Br \xrightarrow{\text{Finely divided Cu/HBr}} ArBr + N_2$$

7.15.9 Iodo Compounds

$$ArN_2Cl + KI(Aq.) \xrightarrow{\text{Boiling}} Ar{-}I + N_2 + KCl$$

7.15.10 Balz–Schiemann Reaction

$$Ar{-}NH_2 \xrightarrow[273\text{–}298\text{ K}]{NaO_2 + HBF_4\ (\text{Fluoroboric acid})} \underset{\text{Tetrafluoroborate salt}}{Ar{-}\overset{\oplus}{N_2}\overset{\ominus}{BF_4}} \xrightarrow{\Delta} ArF + BF_3 + N_2$$

7.15.11 Cyano Compounds

$$ArN_2Cl + KCN \xrightarrow[\text{or Cu powder}]{CuCN} ArCN + N_2 + KCl$$

$$ArN_2Cl + KCN \xrightarrow[K_3[Cu(CN)_4]]{} ArCN + N_2 + KCl$$

7.15.12 Nitro Compounds

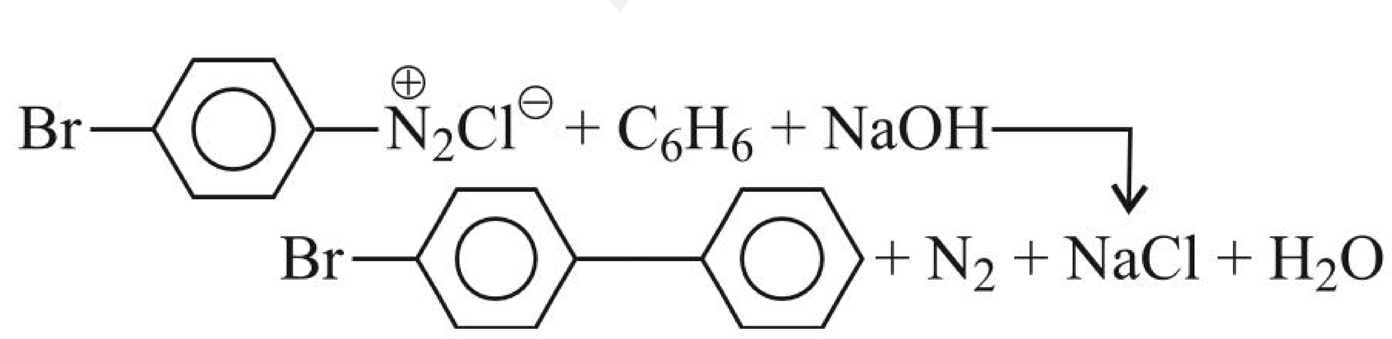
$$ArN_2Cl + HONO \xrightarrow{Cu_2O} ArNO_2 + N_2 + HCl$$

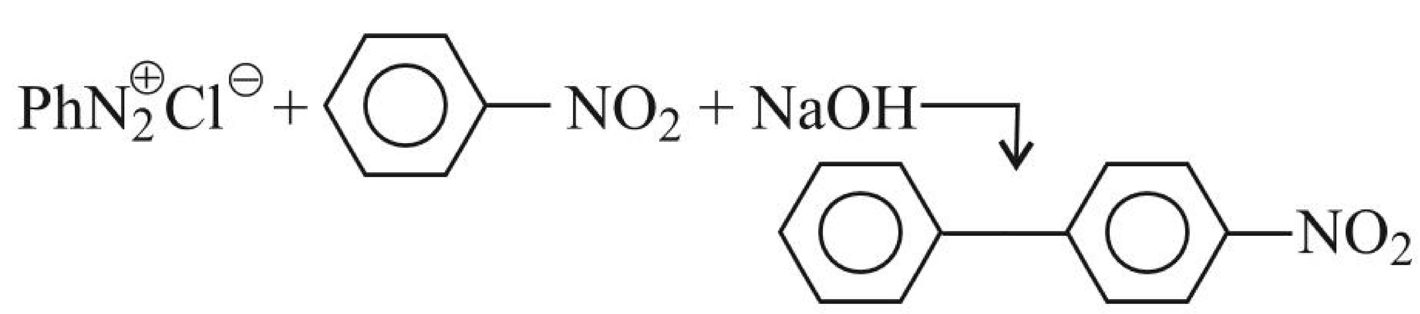
$$ArN_2Cl + CuNO_2 \xrightarrow{\Delta} ArNO_2 + N_2 + CuCl$$

$$Ar\overset{\oplus}{N_2}\overset{\ominus}{BF_4} + NaNO_2 \xrightarrow[\text{Cu powder}]{\Delta} Ar{-}NO_2 + NaBF_4 + N_2$$

7.15.13 Gomberg Reaction (Replacement by Aryl Group)

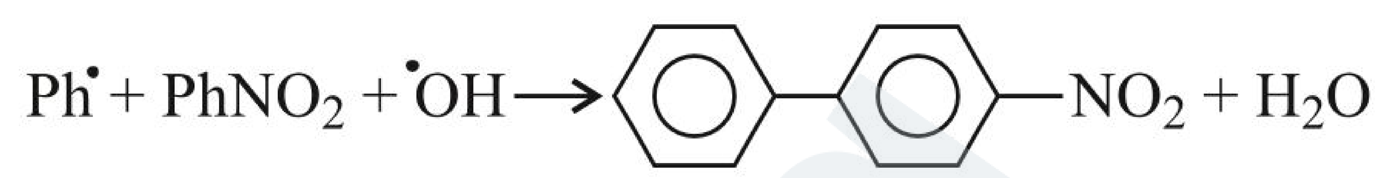
$$ArN_2Cl + \underset{\text{Benzene}}{PhH} + NaOH \longrightarrow \underset{\text{Diphenyl}}{Ar{-}Ar} + N_2 + NaCl + H_2O$$





Whatever is the nature of the substituent in the second component, *o*- and *p*-substitutions occur and the reaction takes place by free radical mechanism.

$$Ph\overset{\oplus}{N_2}Cl^{\ominus} \xrightarrow{\overset{\ominus}{O}H} Ph{-}N{=}N{-}OH \longrightarrow Ph^{\bullet} + N_2 + {}^{\bullet}OH$$



7.15.14 Meerwein Reaction

Diazonium salts add to the compounds containing activated ethylenic bond in acetone solution in the presence of cupric salts to yield halides and loss of N_2 gas (homolytic addition of $Ph^{\bullet}$ at β-position).

I. $PhN_2Cl + CH_2{=}CH{-}CN$ (Acrylonitrile) $\longrightarrow PhCH_2\underset{Cl}{CH}{-}CN$

II.

$$Ph^{\bullet} + CH_2{=}CHCN \longrightarrow PhCH_2\overset{\bullet}{C}HCN$$

$$\xrightarrow{Cu^{2+}} PhCH_2\overset{\oplus}{C}HCN + Cu^{\oplus} \xrightarrow{Cl^{\ominus}} PhCH_2\underset{Cl}{CH}{-}CN$$

III. Addition to α,β-unsaturated acid is accompanied by decarboxylation.

$$ArN_2Cl + \underset{\text{Cinammic acid}}{PhCH{=}CH{-}COOH} \longrightarrow \underset{\text{(Stilbene)}}{PhCH{=}CH{-}Ar} + N_2 + CO_2 + HCl$$

7.15.15 Mechanism

$$PhCH{=}CH{-}COOH \xrightarrow{\overset{\oplus}{Ar}\,\overset{\ominus}{Cl}} Ph{-}\underset{Cl}{CH}{-}\underset{Ar}{CH}{-}COOH \xrightarrow[-HCl]{-CO_2 \text{ and}} Ph{-}CH{=}CH{-}Ar$$

Reduction:

$$Ar{-}N{=}N{-}Cl + 4[H] \xrightarrow{SnCl_2 + HCl} \underset{\text{Phenyl hydrazine hydrochloride}}{Ar{-}NH{-}NH_2.HCl}$$

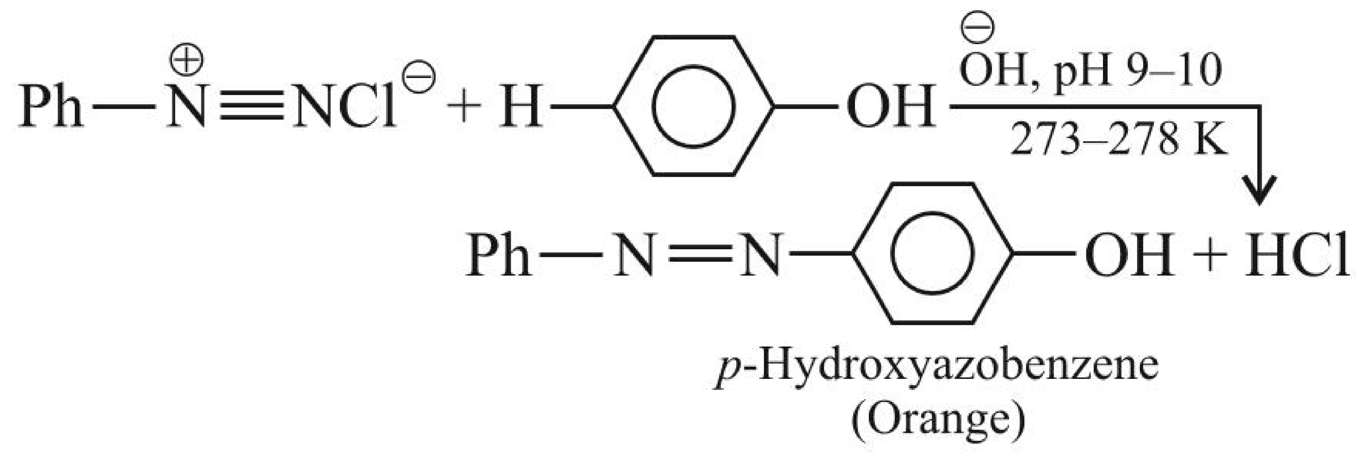
$$Ar{-}N{=}N{-}Cl \xrightarrow[{[H]}]{Zn + HCl} [Ar{-}NH.NH_2] \xrightarrow[{[H]}]{Zn + HCl} Ar{-}NH_2 + NH_3$$

7.16 Reactions Involving Retention of Diazo Group (Coupling Reactions)

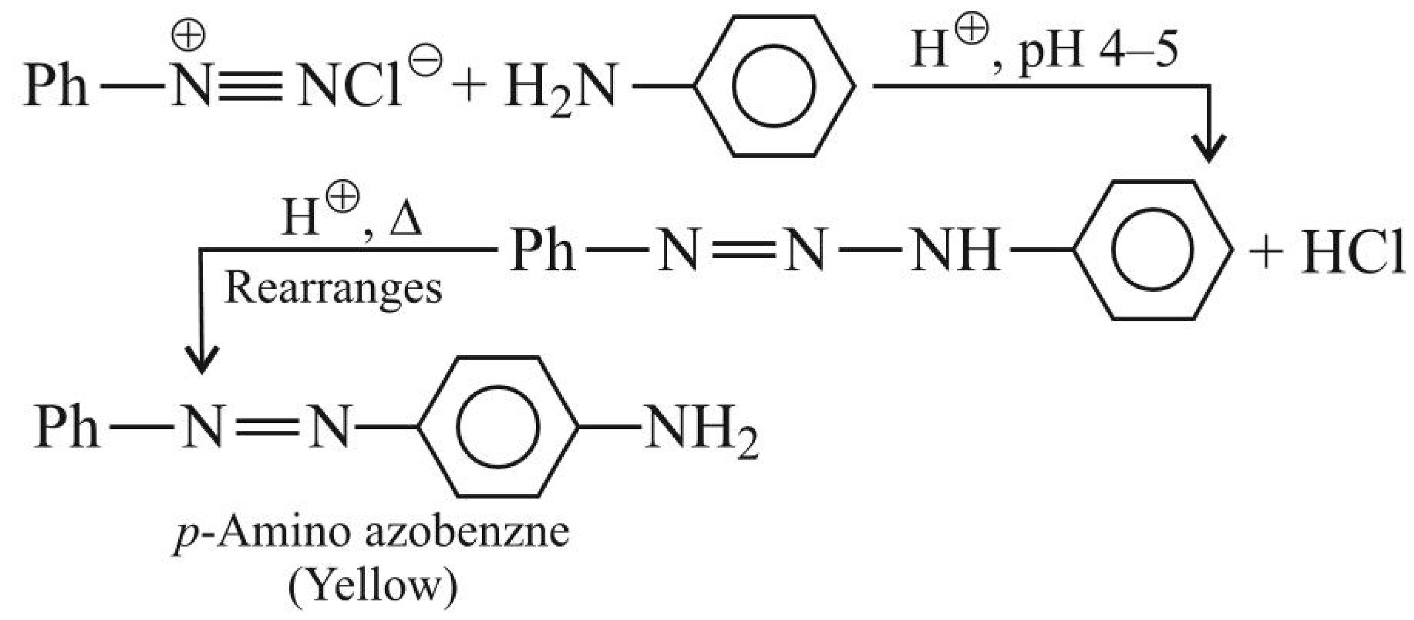
Benzene diazonium salts react with highly reactive (i.e., $\bar{e}$ rich) compounds such as phenols and amines to form brightly coloured

azo compounds. This reaction is called coupling reaction. Coupling with phenols occurs in the basic medium (pH 9–10) and that of amines occur in fairly acidic medium (pH 4–5) at 273–298 K, e.g.,

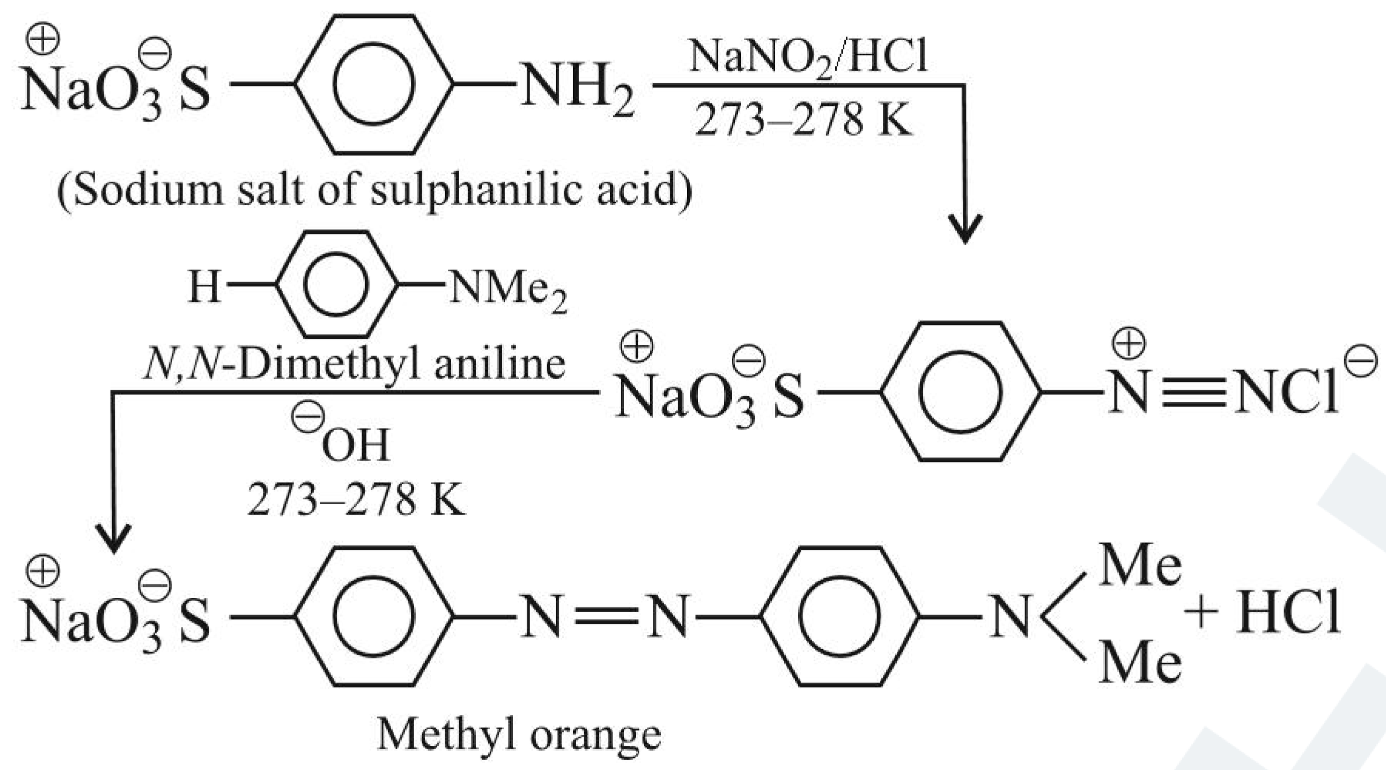
i.



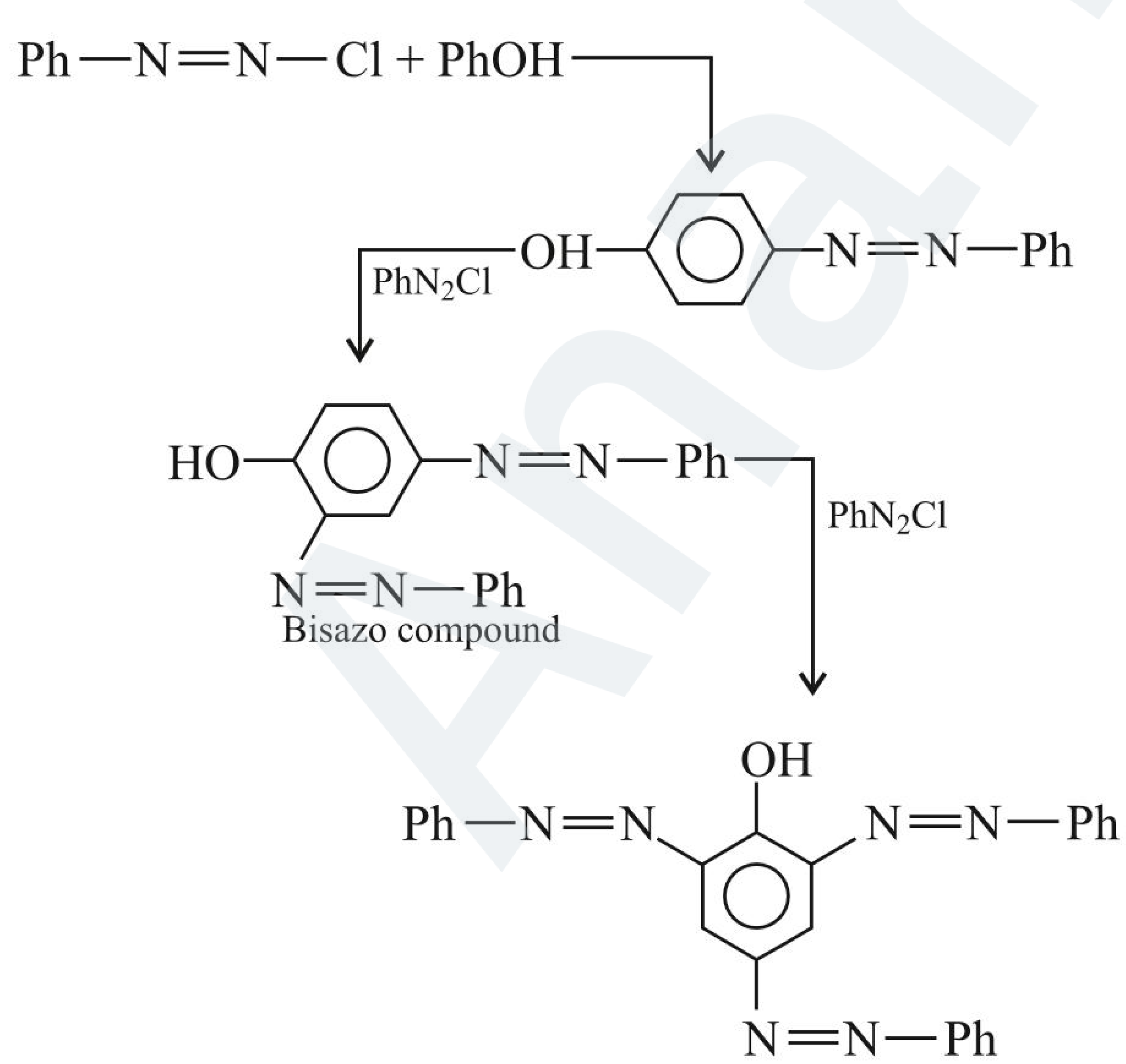
ii.



iii.

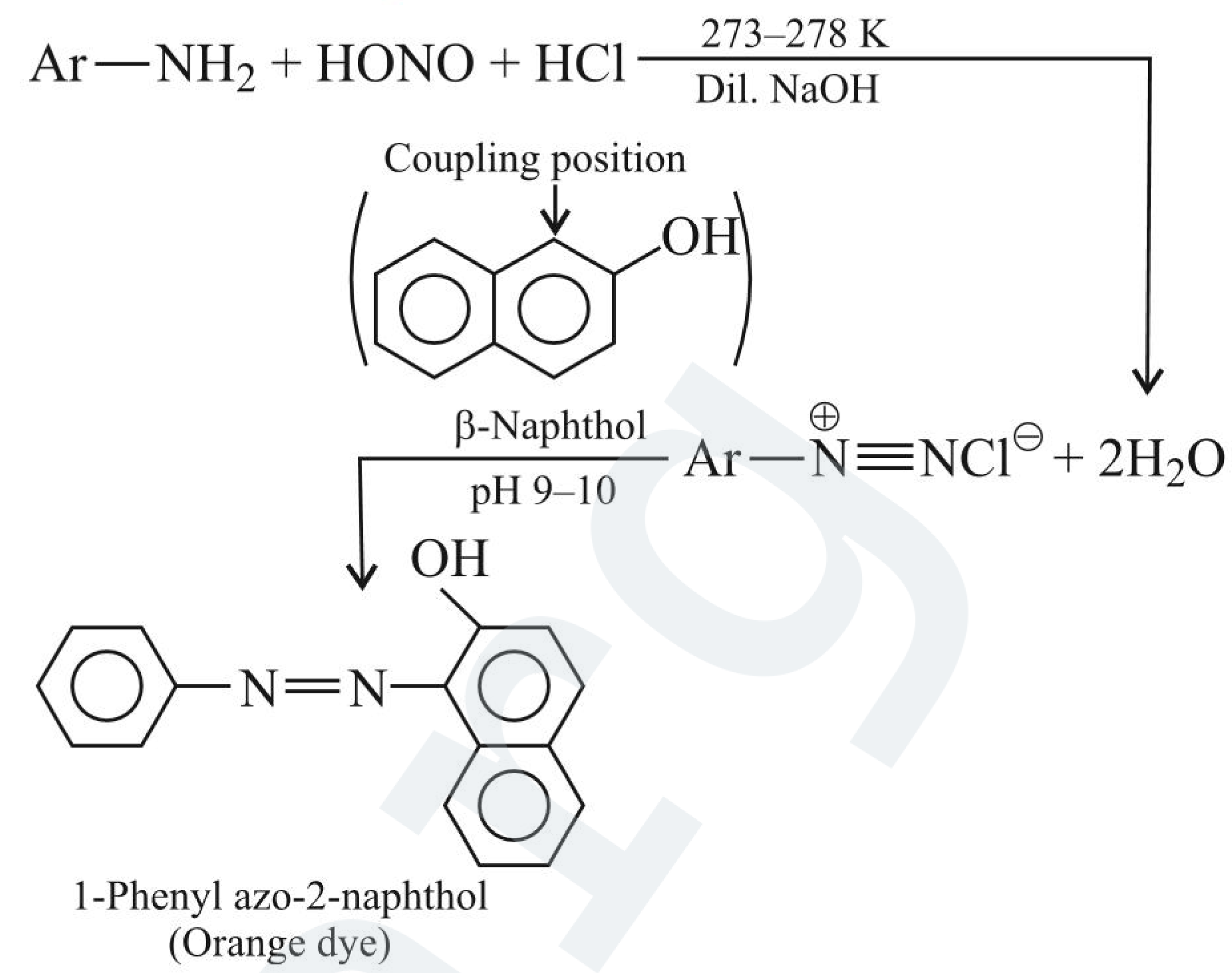


iv. With excess of diazonium salts, the bisazo (*o*- and *p*-) and the trisazo compounds may be produced.

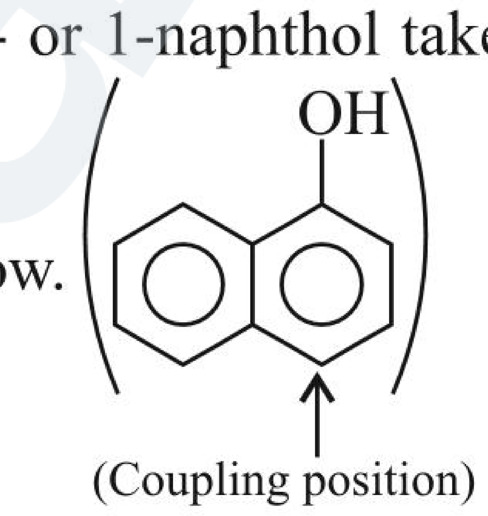


The introduction of a second azo group is facilitated by the presence of an alkyl group in the *para*-position to the hydroxyl group or by two (—OH) groups in the *o*-position.

7.16.1 Dye Test (Test for 1° Aromatic Amine)

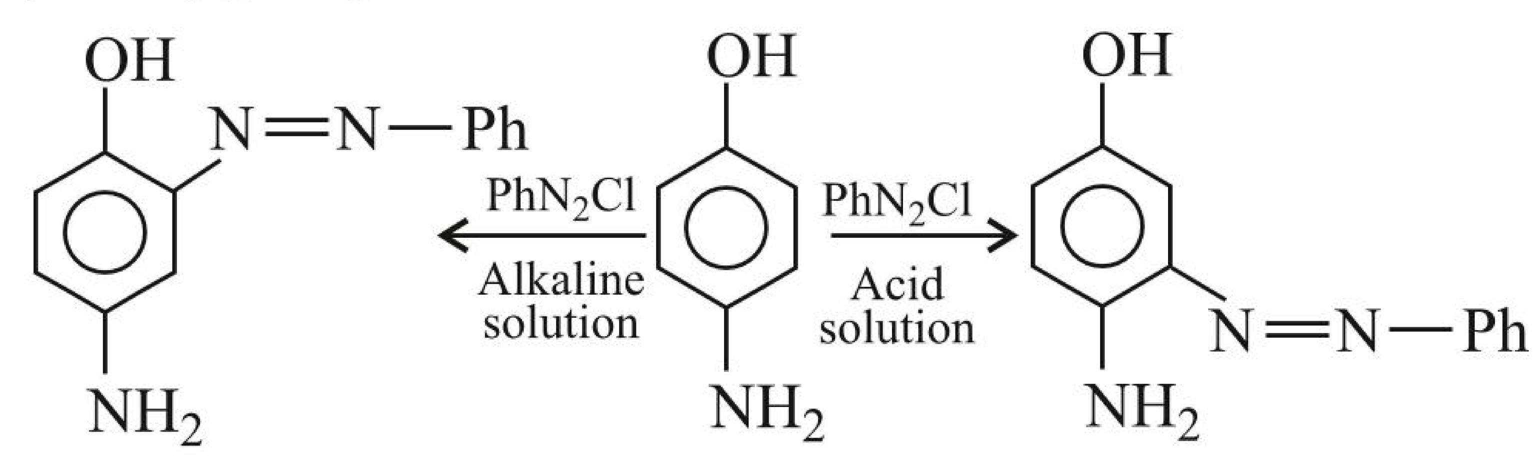


Coupling with α- or 1-naphthol takes place at the position shown by an arrow.

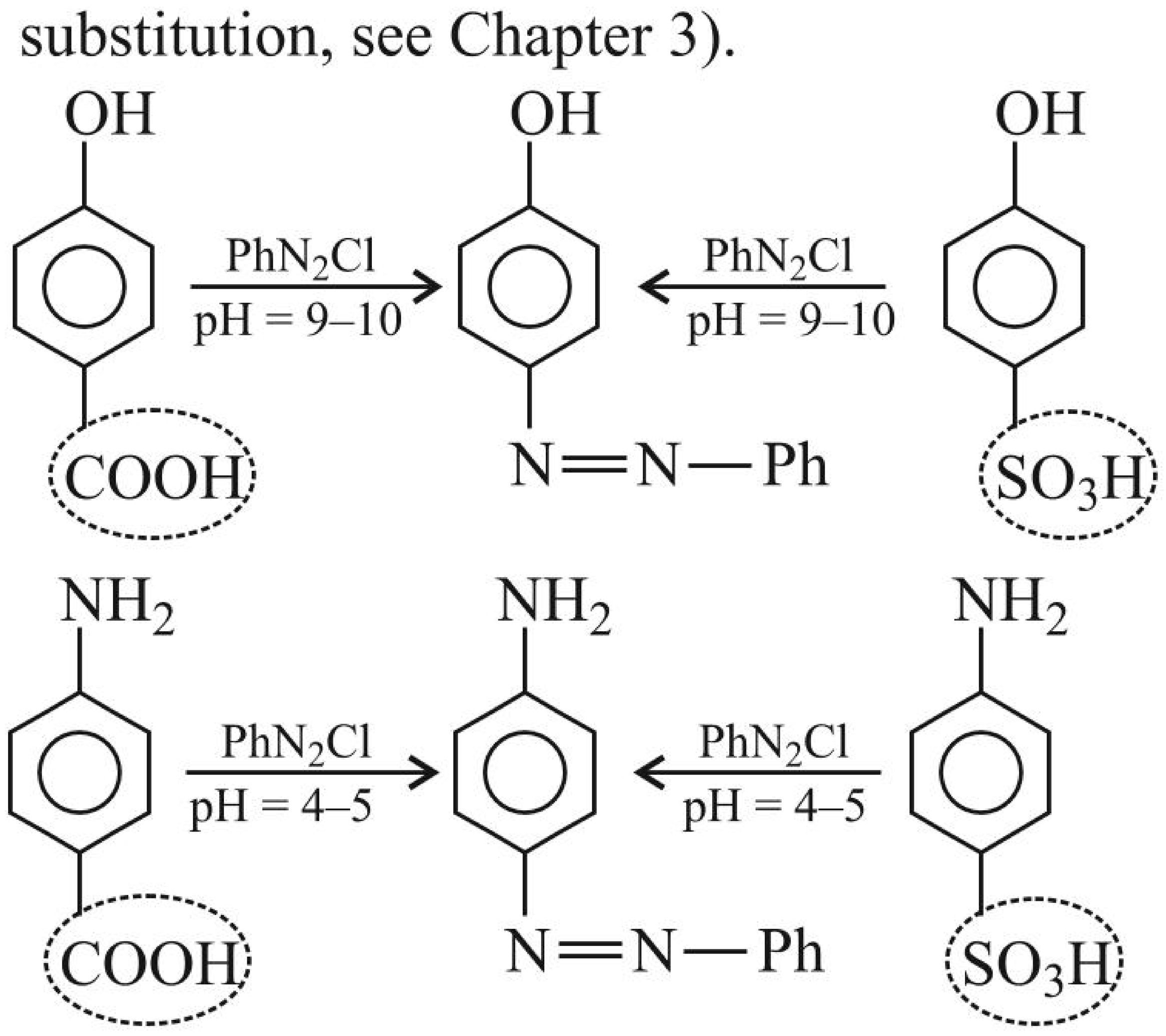


i. In case a compound contains both (—OH) and (—NH_2) groups, the coupling takes place at *o*-position to amino group in acid solution.

In alkaline solution, coupling takes place at *o*-position to (—OH) group.



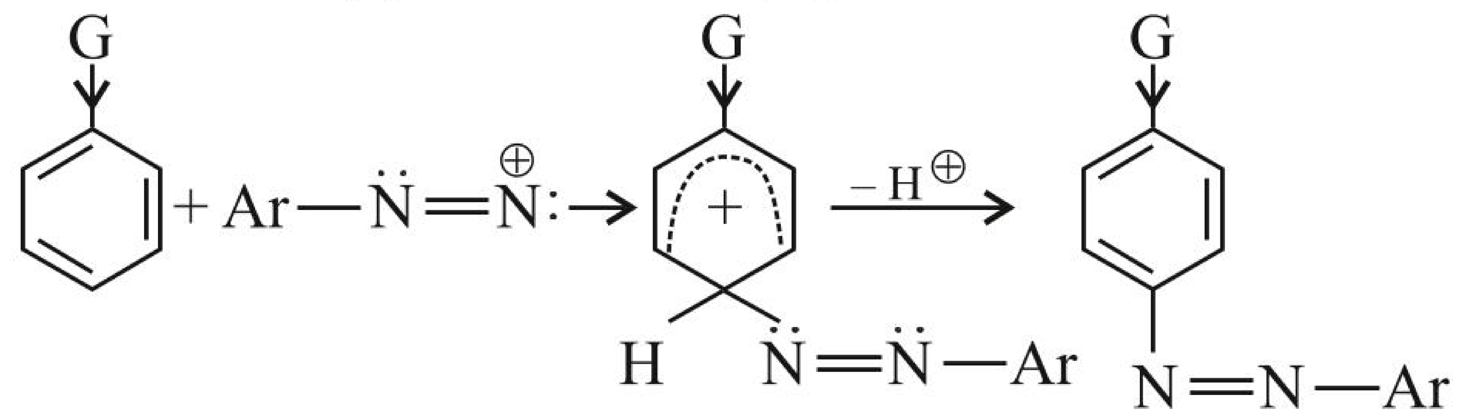
ii. In cases where a (—COOH) or (—SO_3H) group is present at *p*-position to (—OH) or to (—NH_2), it is replaced by the azo group during coupling (it is an example of ipso substitution, see Chapter 3).



7.16.2 Mechanism of Coupling

SE reaction, $Ar\overset{\oplus}{N}_2$ is electrophile. It is a very weak electrophile, so it is capable of attacking only very reactive rings. Coupling is therefore activated by the $\bar{e}$-releasing group, generally (—OH), (—NH_2), (—NHR), or (NR_2). $Ar\overset{\oplus}{N}_2$ is resonance stabilised as shown:

$$Ar-\overset{\oplus}{N}\equiv N: \longleftrightarrow Ar-\ddot{N}=\overset{\oplus}{N}:$$
(I) (II)



Since (II) is the 'reactive' contributing resonating structure, any factor that increases its contribution will increase the reactivity of the diazonium ion. Since the $\bar{e}$-withdrawing group would favour (II) and the $\bar{e}$-donating group would favour (I), therefore the dizonium ion with $\bar{e}$-withdrawing groups is more reactive. Thus, *p*-nitrobenzene diazonium cation is 10,000 times as reactive as *p*-methoxy benzene diazonium ion. Thus, 2,4,6-trinitro benzene diazonium cation is so reactive that it couples with mesitylene.

7.16.3 Coupling Conditions

In the presence of $\overset{\ominus}{O}H$ ion, $Ar\overset{\oplus}{N}_2$ exists in equilibrium with an un-ionised compound (Ar—N═N—OH) and salts $[ArN{=}\ddot{N}^{\oplus}]\overset{\ominus}{O}H$ derived from it, which do not couple.

$$\underset{\text{Couples}}{[Ar-N\equiv N]^{\oplus}\overset{\ominus}{O}H} \underset{H^{\oplus}}{\overset{NaOH}{\rightleftharpoons}} \underset{\substack{\text{Does not couple}\\ \text{(A diazoic acid)}}}{Ar-\dot{N}=N-OH}$$

$$\Big\Updownarrow \; H^{\oplus} / NaOH$$

$$\underset{\substack{\text{Does not couple}\\ \text{(A diazotate anion)}}}{Ar-\dot{N}=N-\overset{\ominus\,\oplus}{ONa}}$$

Therefore, coupling does not take place in strong basic condition.

Strong acid converts $ArNH_2$ to $Ar\overset{\oplus}{N}H_3$, whose ring is deactivated due to coupling, so strong acidic conditions are also not required. Hence amines couple fastest in mild acidic conditions.

Phenol exists in equilibrium with phenoxide ion.

$$\underset{\text{Couples slowly}}{PhOH} \underset{H^{\oplus}}{\overset{\overset{\ominus}{O}H}{\rightleftharpoons}} \underset{\text{Couples rapidly}}{PhO^{\ominus}}$$

Due to high $\bar{e}$-donating power of $O^{\ominus}$ than OH, phenoxide ion is more reactive than phenol. Therefore, the higher the acidity of the medium, the lower the reactivity of the phenoxide ion is.

Therefore, conditions for coupling can be summarised as follows:

I. The solution must be so alkaline that the concentration of diazonium ion is too low.

II. It must not be so acidic that the concentration of free amine or phenoxide ion is too low.

That is why amines couple fastest in mild acidic solution and phenols couple fastest in mild alkaline solution.

Coupling is better in the following cases:

I. The more EWG ($\bar{e}$-withdrawing group) in diazonium ion, the faster the coupling is.

II. The more EDG ($\bar{e}$-donating group) in coupling compound, the faster the coupling is.

III. $ArN_2^{\oplus}$ is weak electrophile which undergoes diazo coupling only with the ring activated by (—OH), (—NH_2), (—NHR), or (—NR_2).

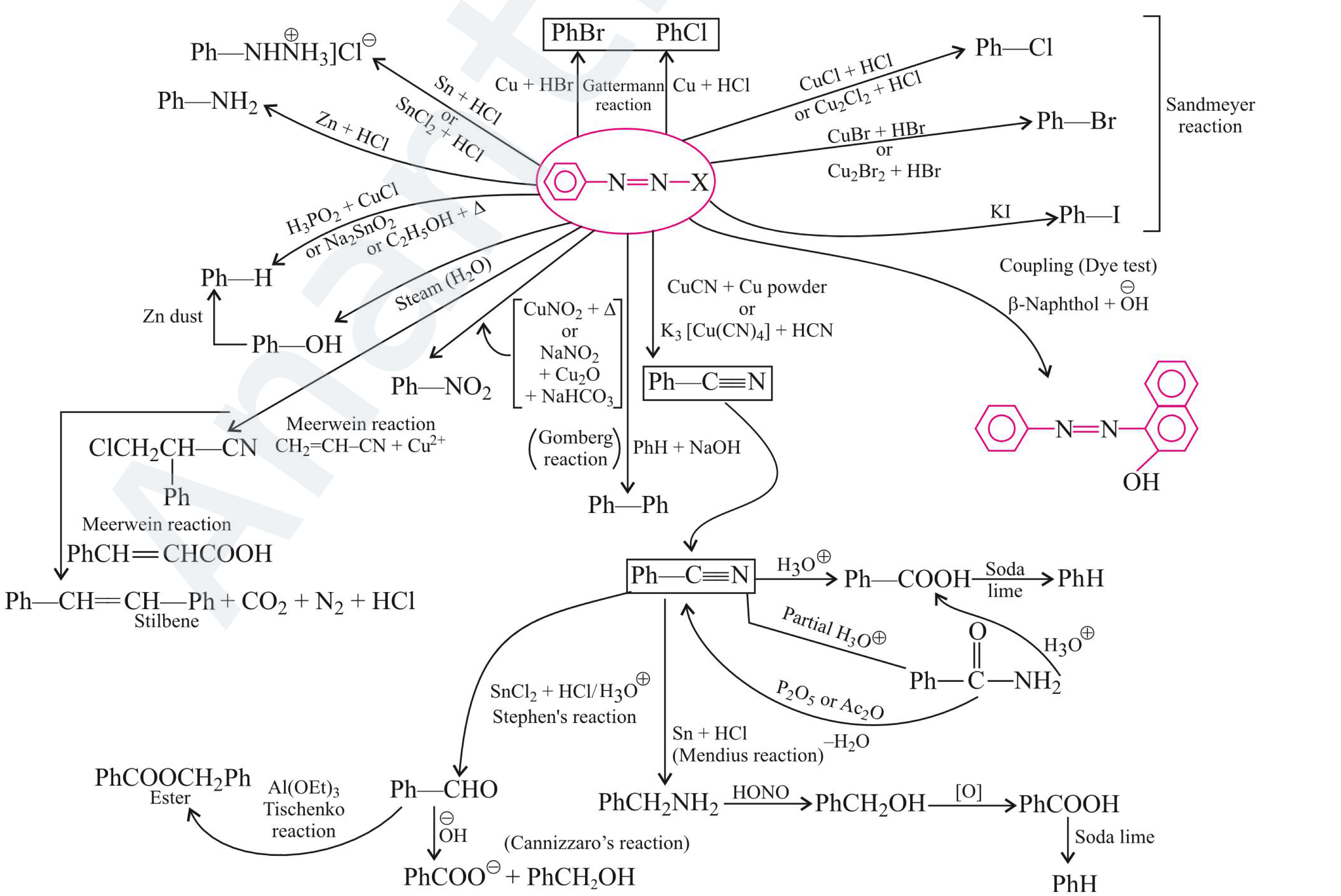


Fig. 7.4 Reactions of diazonium salts

Illustration 7.14

Give the decreasing order of reactivity of diazonium ion coupling with phenol.

a. **I.** $p\text{-}NO_2\text{—}C_6H_4\overset{\oplus}{N}_2$ **II.** $p\text{-}Cl\text{—}C_6H_4\overset{\oplus}{N}_2$
III. $C_6H_5\overset{\oplus}{N}_2$ **IV.** $p\text{-}Me\text{—}C_6H_4\overset{\oplus}{N}_2$
V. $p\text{-}MeO\text{—}C_6H_4\overset{\oplus}{N}_2$

b. **I.** $p\text{-}NO_2\text{—}C_6H_4\overset{\oplus}{N}_2$ **II.** $m\text{-}NO_2\text{—}C_6H_4\overset{\oplus}{N}_2$
III. $p\text{-}Cl\text{—}C_6H_4\overset{\oplus}{N}_2$ **IV.** $m\text{-}Cl\text{—}C_6H_4\overset{\oplus}{N}_2$
V. $Ph\overset{\oplus}{N}_2$

c. **I.** $m\text{-}NO_2\text{—}C_6H_4\overset{\oplus}{N}_2$ **II.** $m\text{-}MeO\text{—}C_6H_4\overset{\oplus}{N}_2$
III. $p\text{-}MeO\text{—}C_6H_4\overset{\oplus}{N}_2$ **IV.** $o\text{-}MeO\text{—}C_6H_4\overset{\oplus}{N}_2$
V. $Ph\overset{\oplus}{N}_2$

Sol. The more EWG in diazonium ion, the faster the coupling is.

a. (I) > (II) > (III) > (IV) > (V)
(I) ⇒ (p-NO_2, – I, and – R), (II) ⇒ (p-Cl, –I),
(III) ⇒ Standard
(IV) ⇒ (p-Me, +I, and H.C.),
(IV) ⇒ [p-MeO—, – I, and + R, net ED power of MeO— is greater than ED power of (Me—) group].

b. (I) > (II) > IV > (III) > (V)
(I) ⇒ (p-NO_2, – I, and – R),
(II) ⇒ (m-NO_2, only – I),
(IV) ⇒ (m-Cl, – I, but – I at $m > p$ and – I of NO_2 > – I of Cl).
(III) ⇒ (p-Cl, – I,), (V) ⇒ Standard

c. (I) > (II) > (V) > (IV) > (III)
(I) ⇒ (m-NO_2, only – I), (II) ⇒ (m-MeO—, only – I),
(V) ⇒ Standard, (IV) ⇒ (o-MeO, – I, and + R, net ED)
(III) ⇒ [p-MeO—, –I, and + R, but – I at p- < o-, so net ED power of (III) > (IV)]

Illustration 7.15

Give the decreasing order of reactivity for the following coupling compounds with PhN_2Cl.

a. **I.** Aniline **II.** Phenol
III. Toluene **IV.** Chlorobenzene
V. Nitrobenzene

b. **I.** Toluene **II.** Ethyl benzene
III. Cumene **IV.** t-Butyl benzene
V. Anisole

Sol. The more EDG in coupling compound, the faster the coupling is.

a. (I) > (II) > (III) > (IV) > (V)
ED power of: $—\ddot{N}H_2 > —\ddot{O}H > Me— > —Cl > —NO_2$

b. (V) > (I) > > (II) > (III) > (IV)
ED power of: $—\ddot{O}Me$ > —Me (Three H.C. structures and +I)
> $—CH_2CH_3$ (two H.C. structures and +I)
> $Me_2CH—$ (isopropyl) (one H.C. structure and +I)
> $Me_3C—$ (t-butyl) (No H.C.; only +I)

Note: Coupling does not take place with any of the compounds (I) to (IV) in (b) and (III) to (V) in (a), since the ring is insufficiently activated. $ArN_2^{\oplus}$ is a weak electrophile which undergoes diazo coupling only with the ring activated by (—OH), (—NH_2), (—NHR), or (—NR_2), but in the problem the decreasing order of coupling has been asked, so the decreasing order is given according to their activating power.

Illustration 7.16

Explain why 2,4-dinitrobenzene diazonium ion couples with anisole but $PhN_2^{\oplus}$ does not. Write the coupling reaction.

Sol. The ring is not sufficiently activated by —OMe group for it to react with most $PhN_2^{\oplus}$. However, $\bar{e}$-withdrawing (—NO_2) groups make this diazonium ion less stable and thus more reactive than $PhN_2^{\oplus}$.

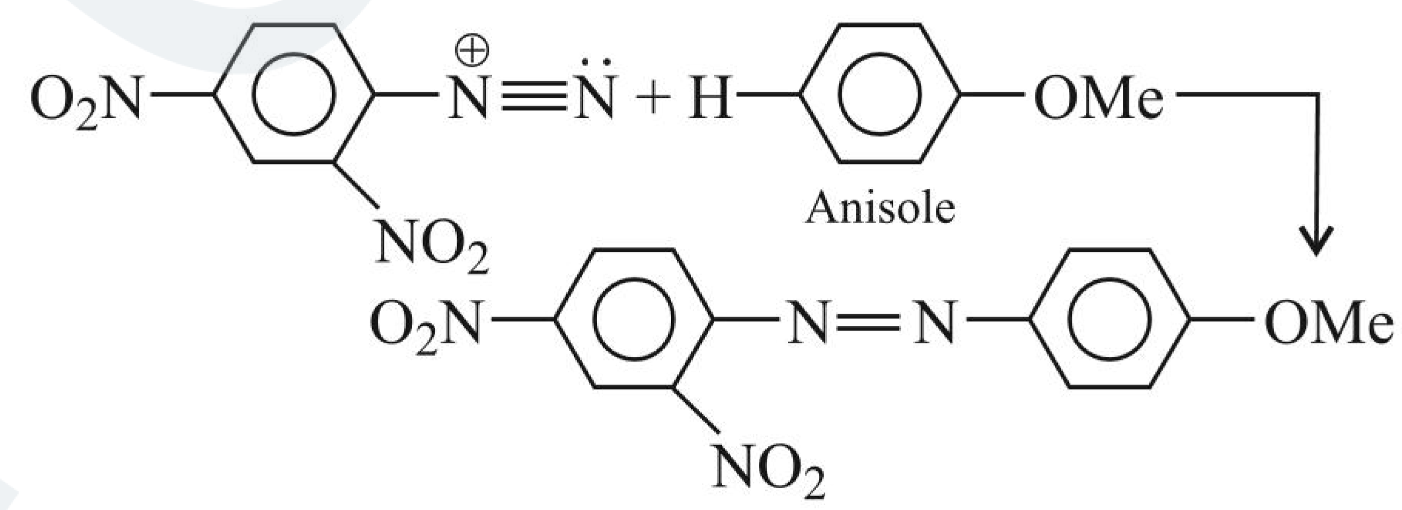


Illustration 7.17

Synthesise benzylamine ($PhCH_2NH_2$) by

a. Hofmann degradation **b.** Reductive amination
c. Alkyl halide amination **d.** Gabriel method
e. Nitrile reduction

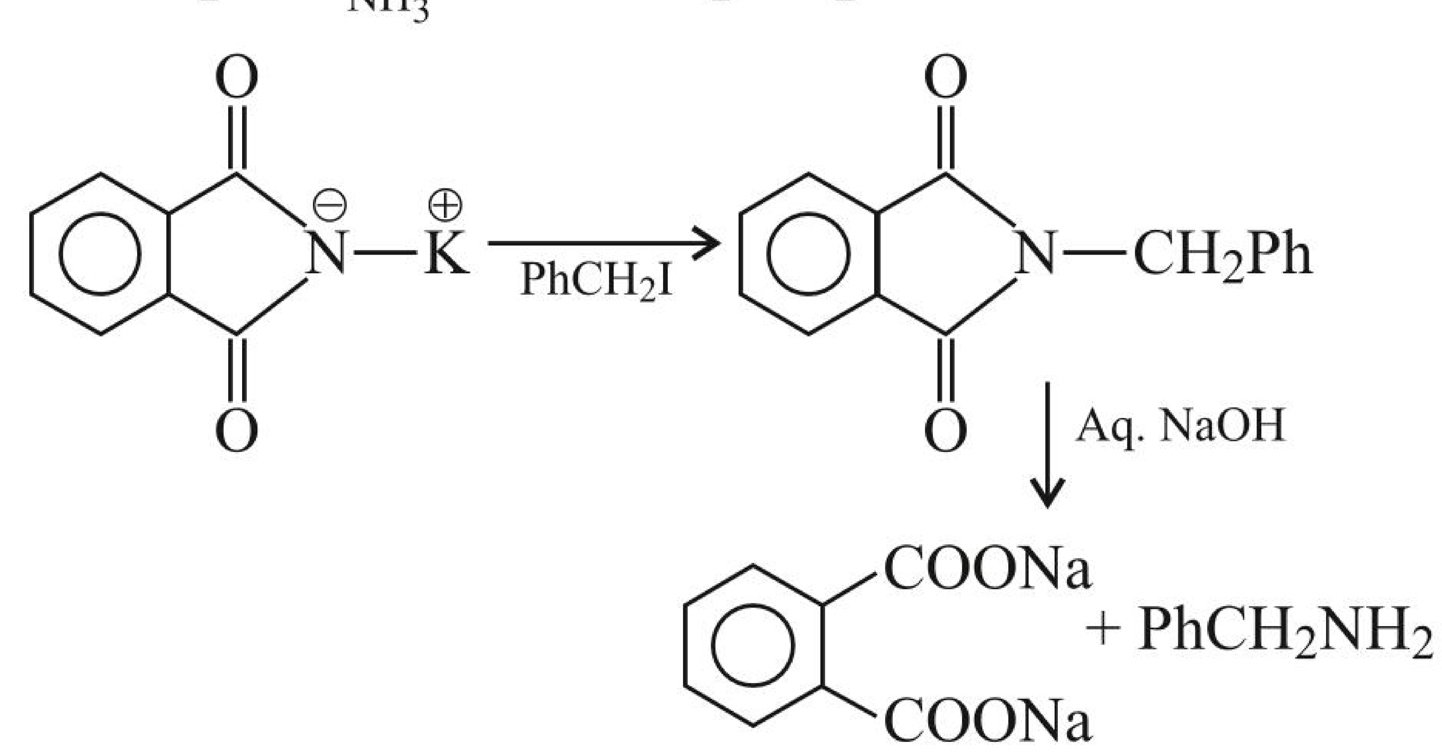
Sol.

a. $PhCH_2\text{—}\overset{O}{\overset{\|}{C}}\text{—}NH_2 \xrightarrow{Br_2,\ NaOH} Ph\,CH_2NH_2$

b. $PhCH{=}O + H_2NH \longrightarrow PhCH{=}NH \xrightarrow[\text{NaCNBH}_3]{H_2/Ni \text{ or}} PhCH_2NH_2$

c. $PhCH_2I \xrightarrow[NH_3]{\text{Excess}} Ph\,CH_2NH_2$

d.



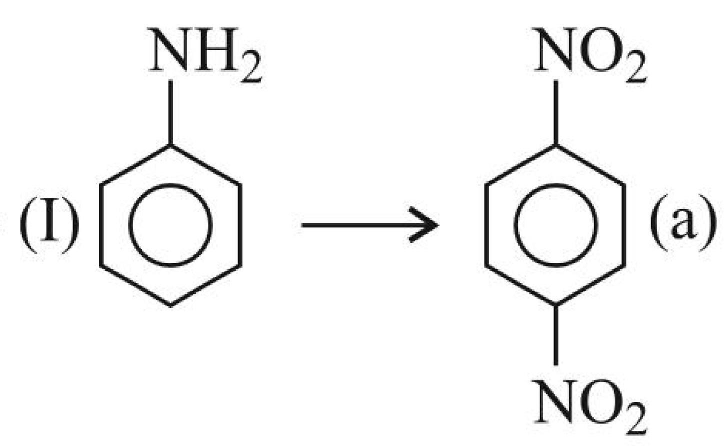
e. $Ph\text{—}C\equiv N \xrightarrow[H_2O]{LAH} Ph\,CH_2NH_2$

ILLUSTRATION 7.18

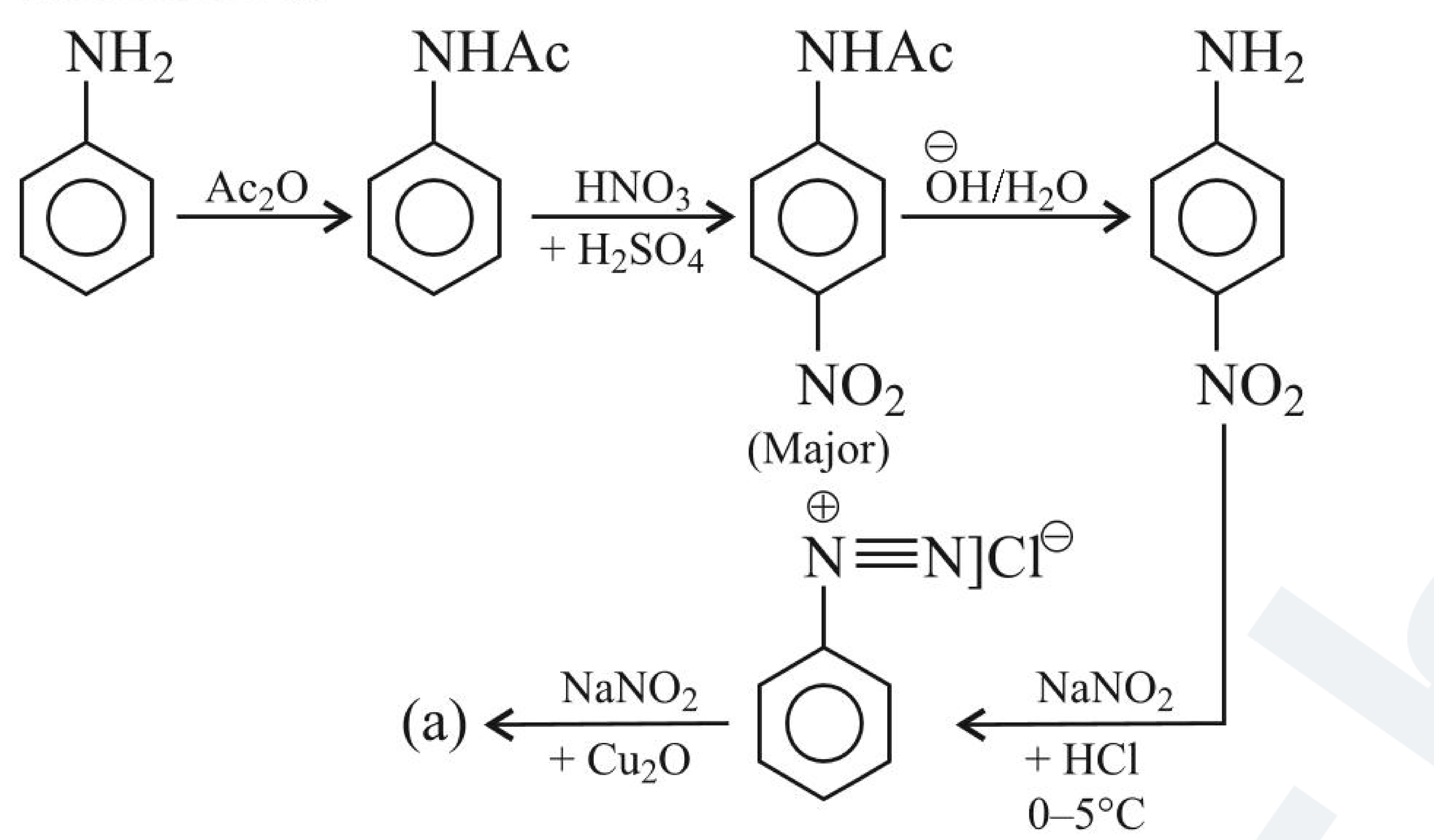
Starting from benzene or toluene or aniline and with the aid of diazonium salt synthesise the following:

a. *p*-Nitrobenzene **b.** *o*-Bromotoluene
c. 1,3,5-Tribromobenzene **d.** *m*-Bromotoluene
e. *m*-Bromochlorobenzene

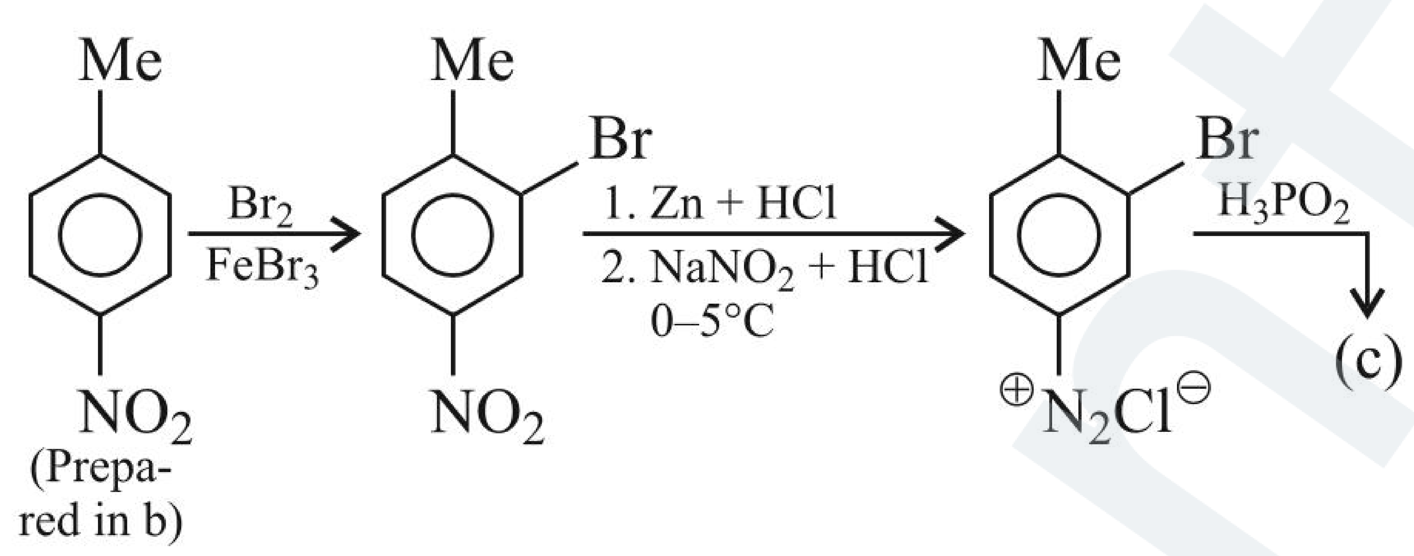
Sol. **a.**



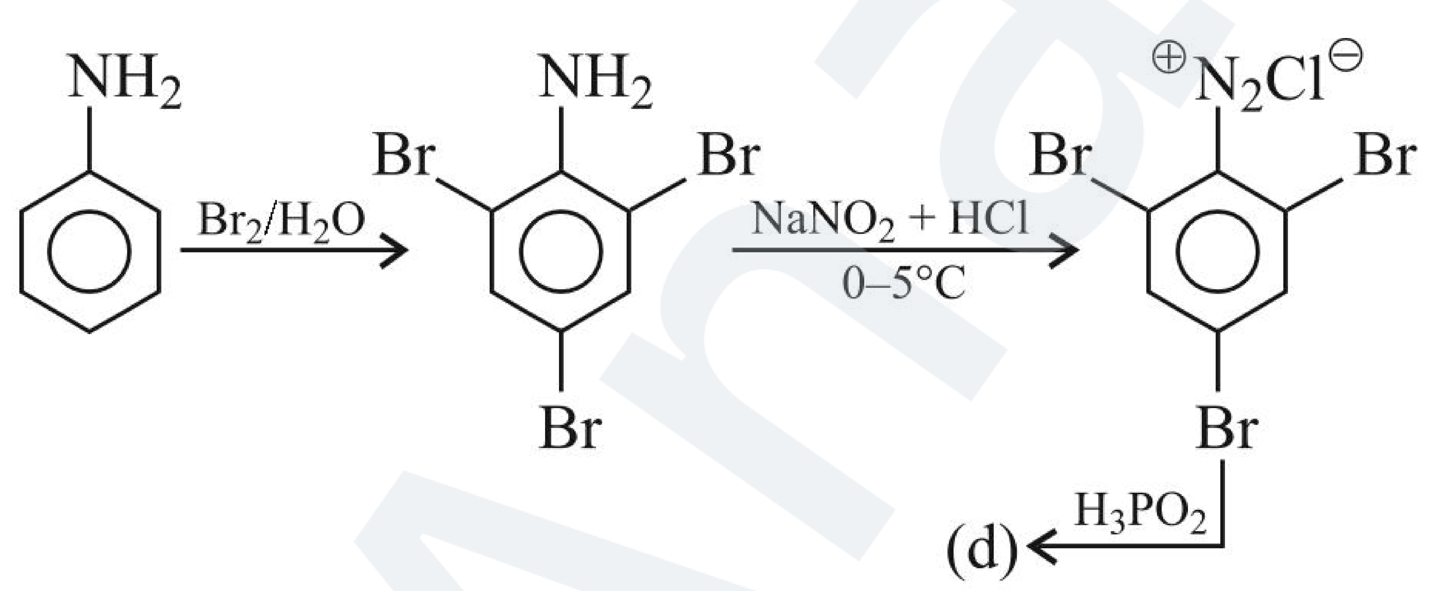
Here, —NH_2 is *o*- and *p*-directing; introduce one (—NO_2) group, directly by nitration after protecting (—NH_2) group (direct nitration of aniline would yield mixture and tarry products. Introduce the second (NO_2) group *via* diazonium salt method.



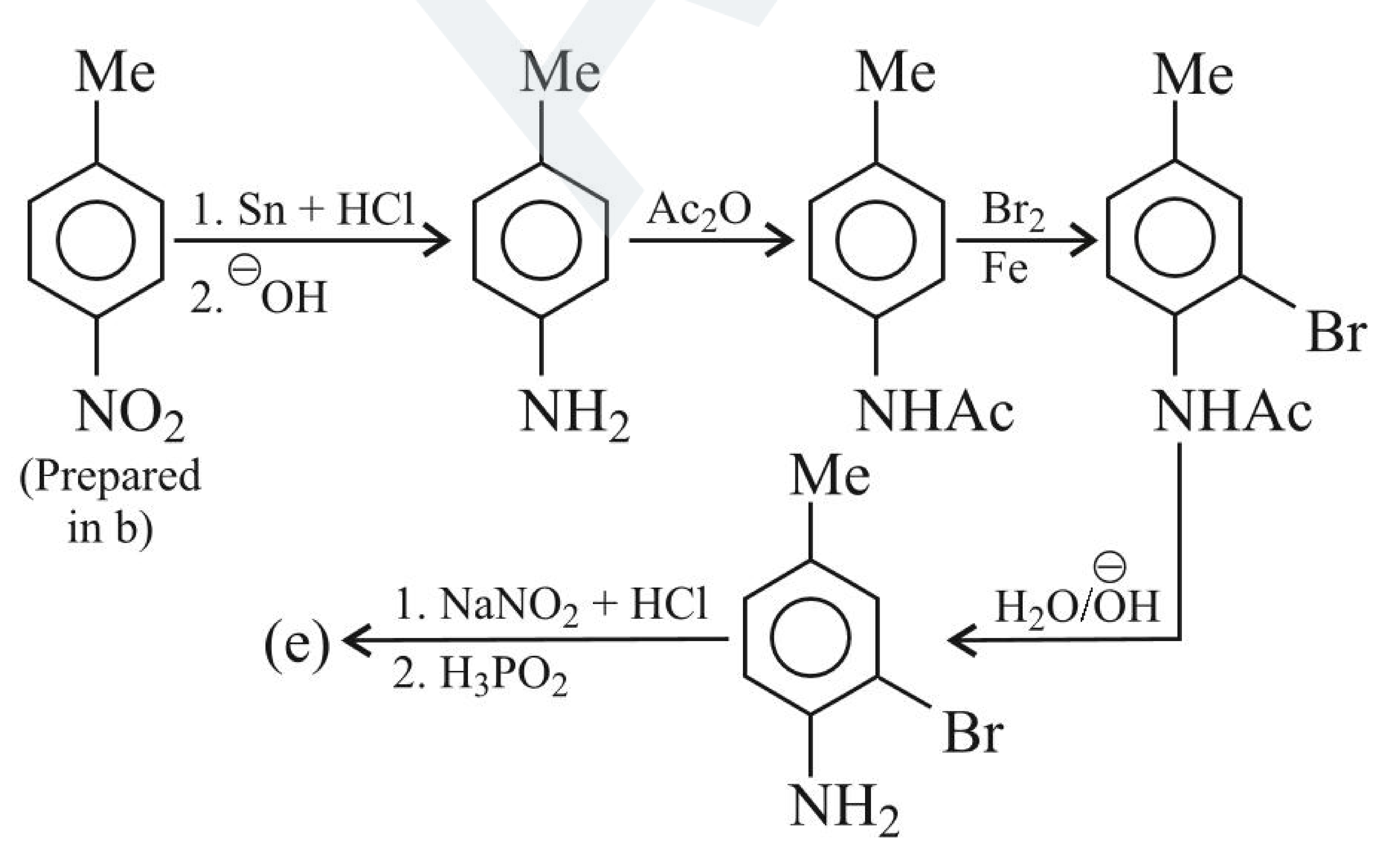
b.



c.



d.



e.

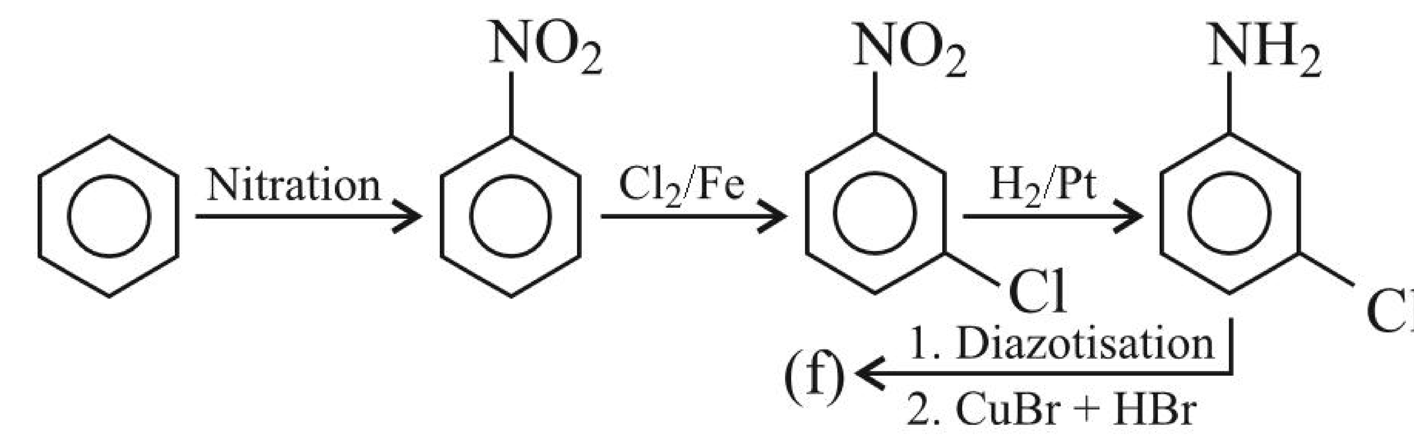
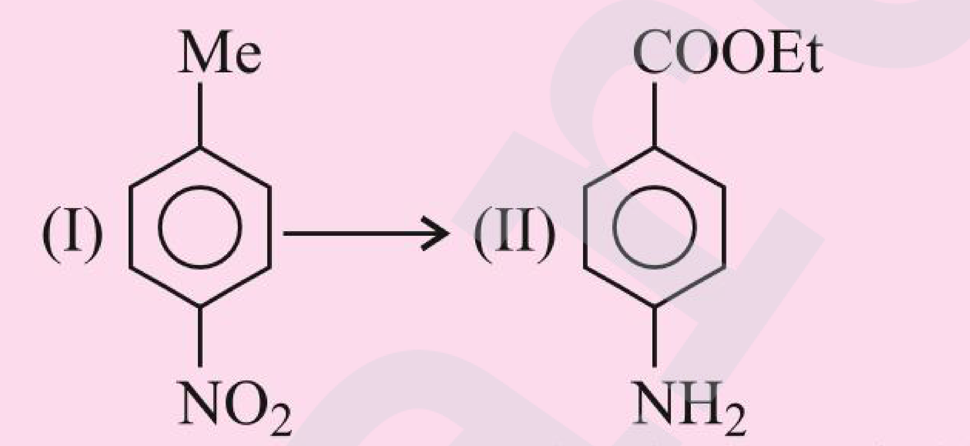


ILLUSTRATION 7.19

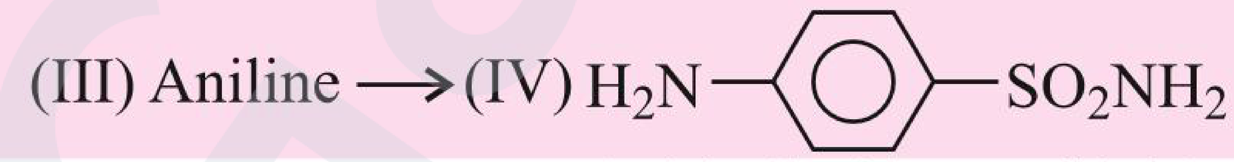
Convert the following:

a.



(Benzocain, a local anaesthetic)

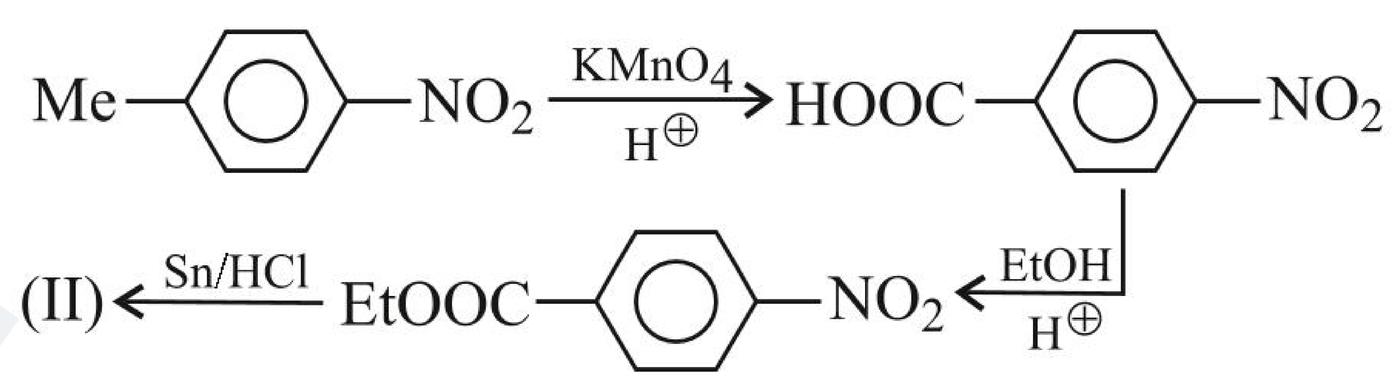
b.



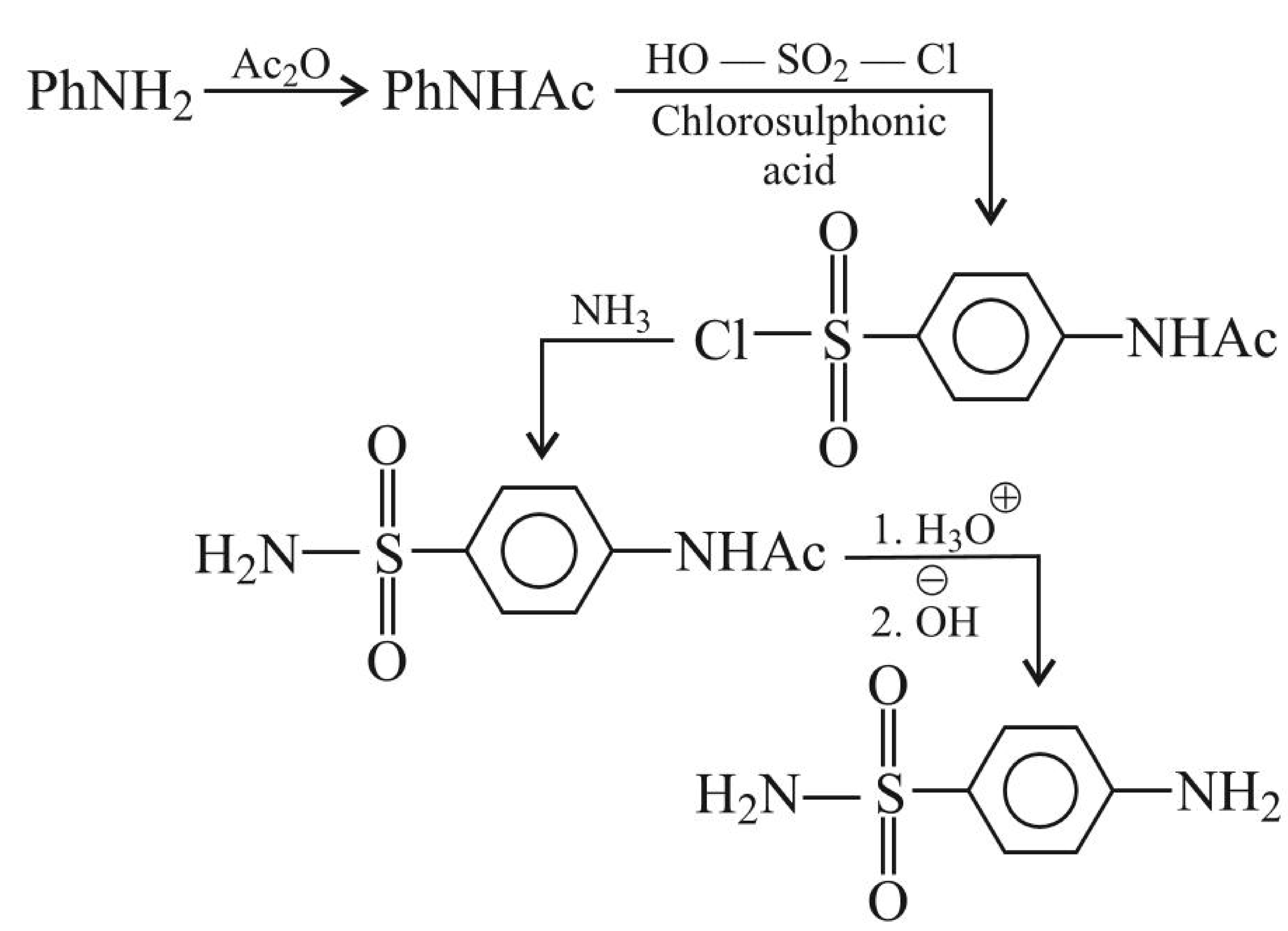
(Sulphanilamide, an antibiotic)

Sol.

a.



b.



CONCEPT APPLICATION EXERCISE 7.2

1. Identify (A) and (B).

An optically active amine (A) $\xrightarrow[\text{methylation and elimination}]{\text{Hofmann exhaustive}}$ (B) (Alkene) $\xrightarrow{O_3/\text{Red.}}$ HCH = O + Butanal

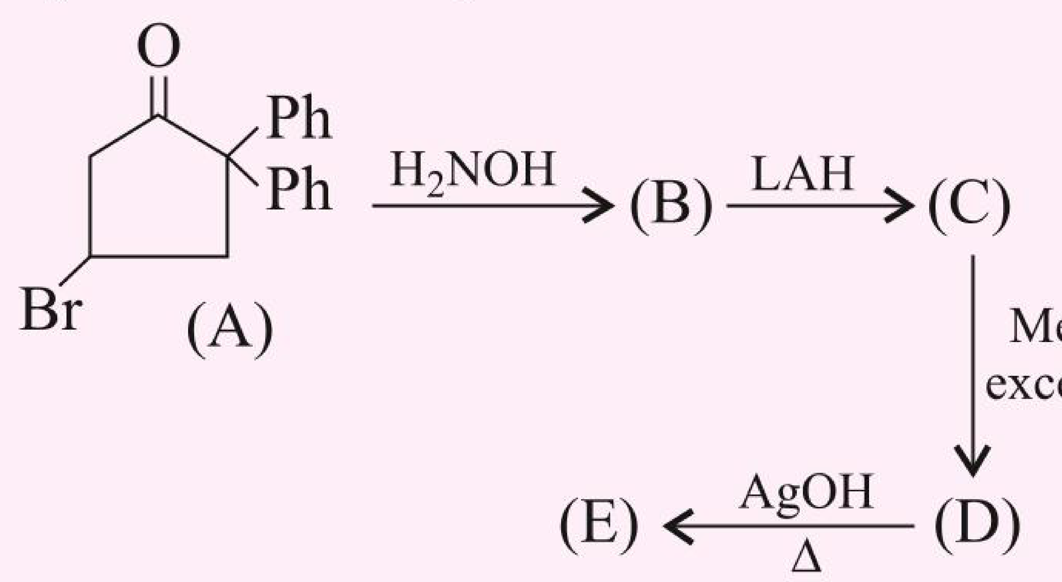
2. Identify (A) to (E) and write chemical equations for the various reactions involved.

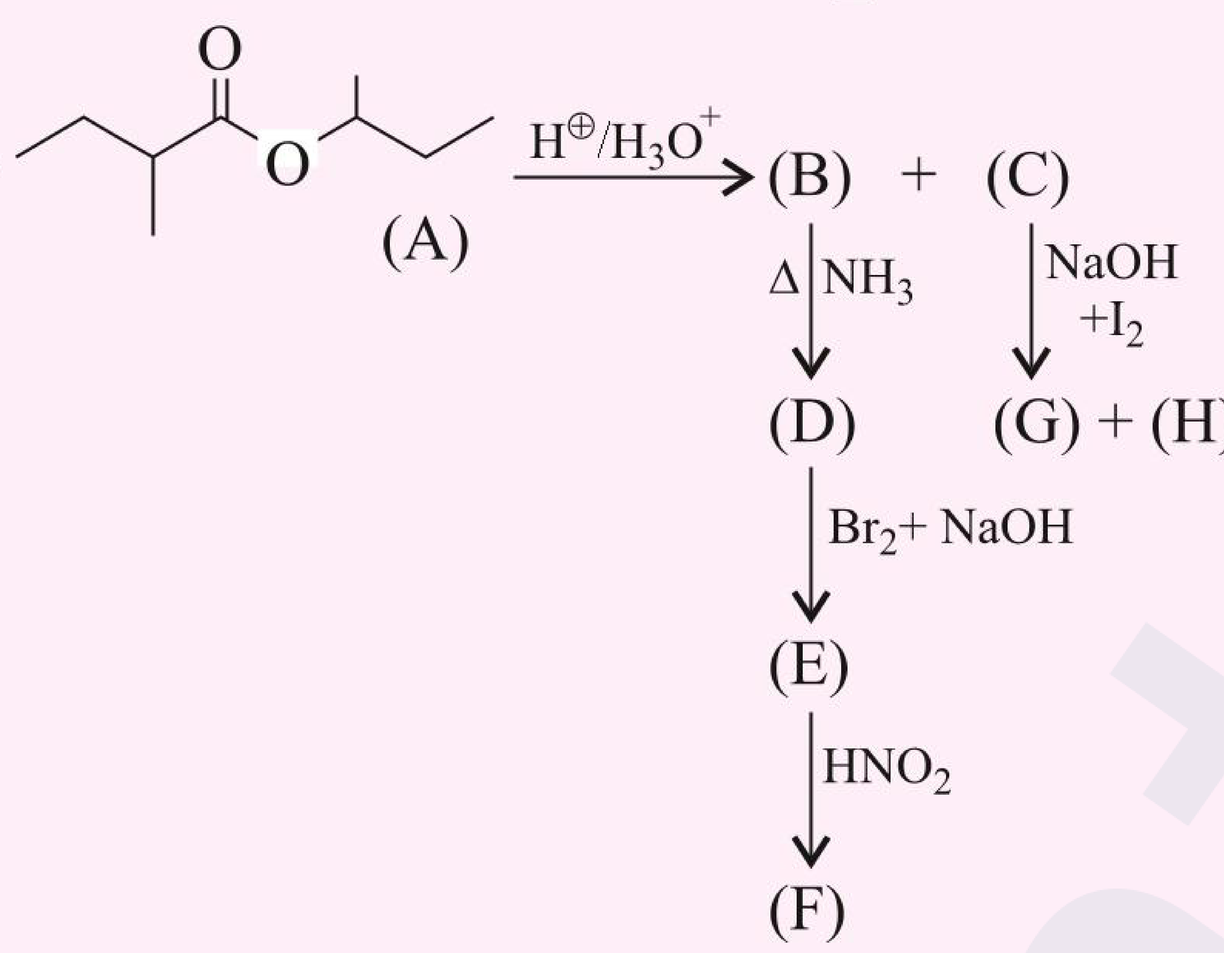
$$\underset{\text{Forms salt with acid}}{(A)\ (C_6H_7N)} \xrightarrow[\text{MeOH + }H_2SO_4,\ \Delta]{\text{Excess of}} (B)\ (C_8H_{11}N) \xrightarrow{HNO_2} C_8H_{10}N_2O\ (C) \xrightarrow{\text{Boiling with NaOH}} C_6H_5O_2N\ (D)$$

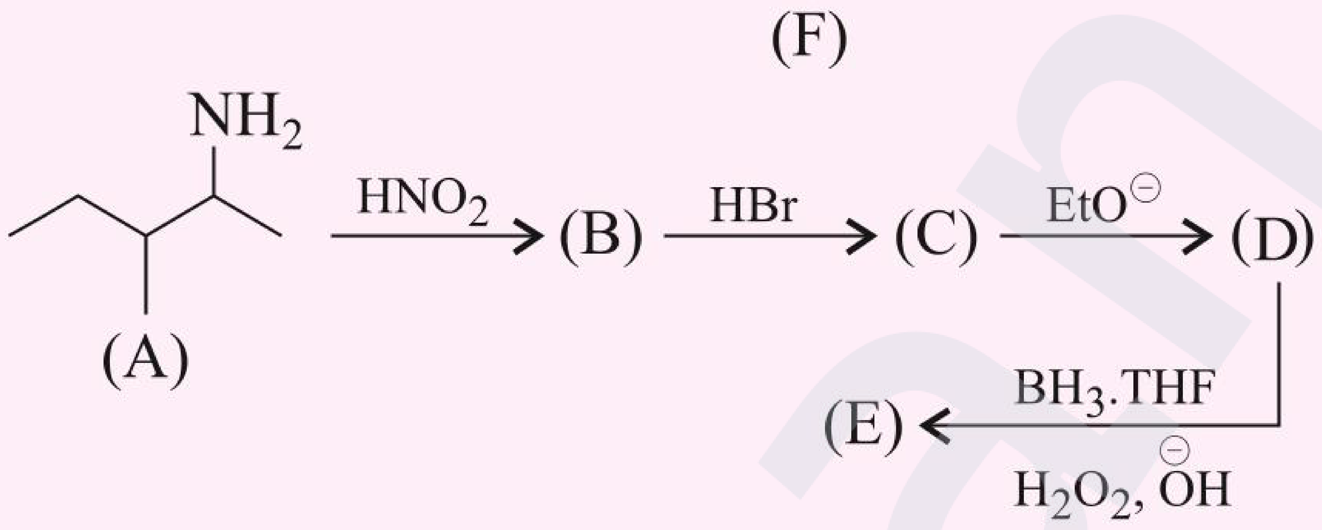
$$(B) \xrightarrow{HCl} \text{Hydrochloride salt of (B)} \xrightarrow{\text{Heat, 570 K}} (E)\ \text{[Isomeric compound of the hydrochloride salt of (B)]}$$

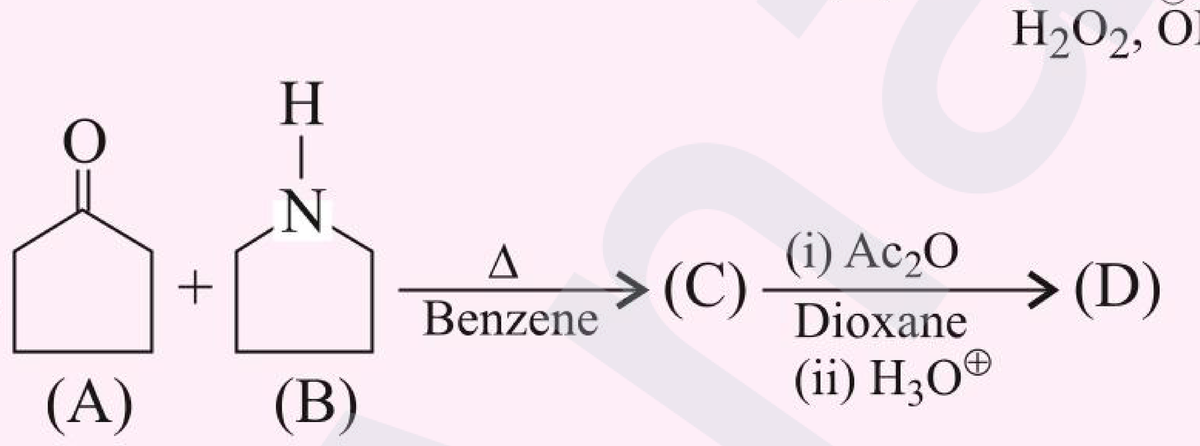
$$(F) \xleftarrow{\overset{\ominus}{O}H} (E)$$

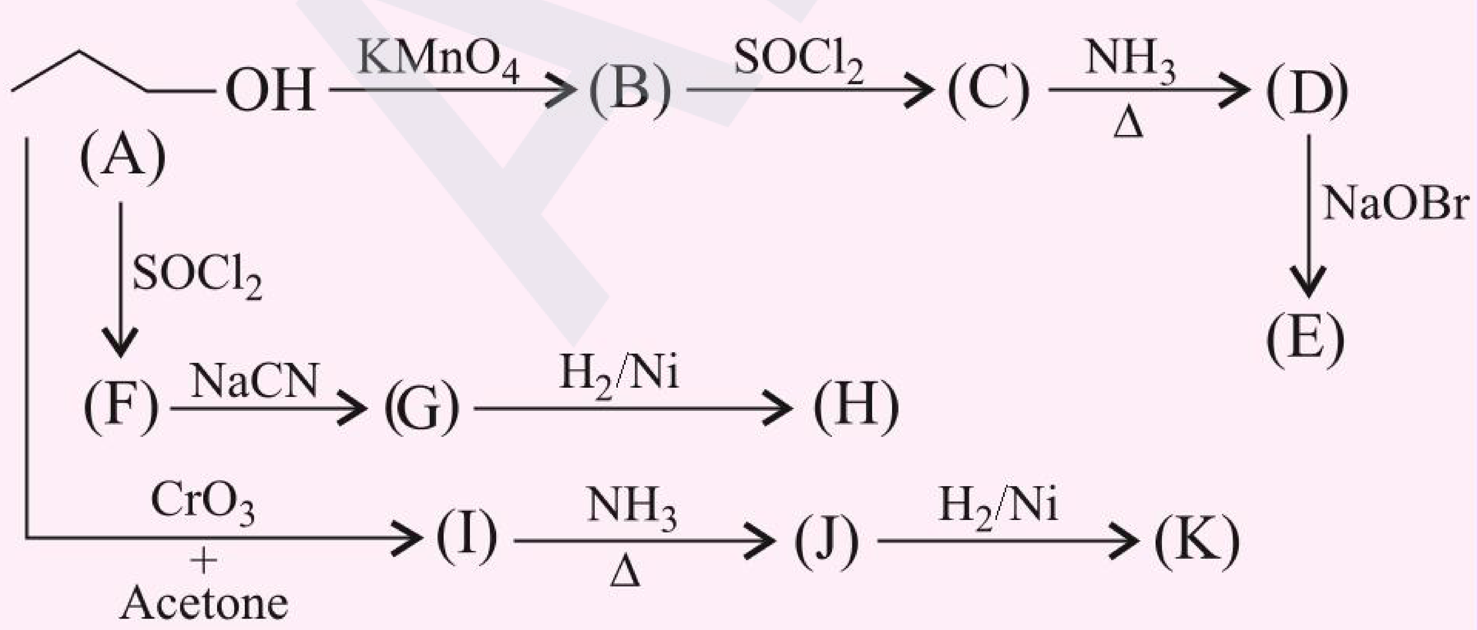
3. Identify the reactants & products.

a. 

b. 

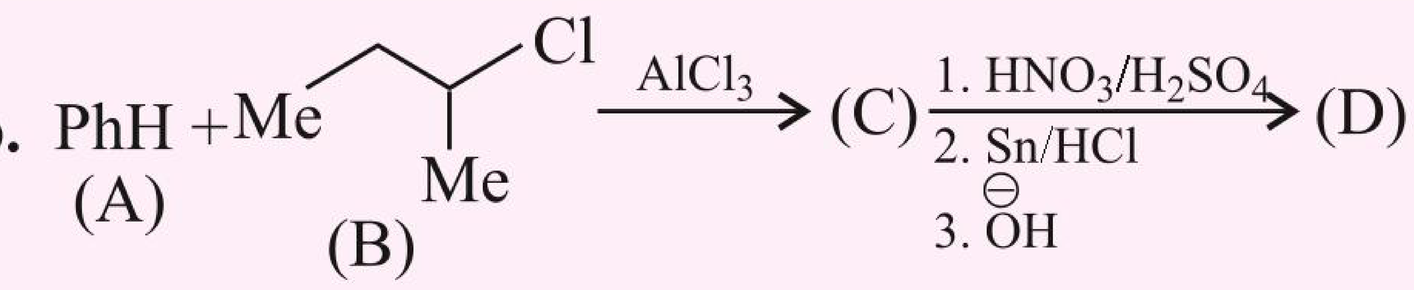
c. 

d. 

e. 

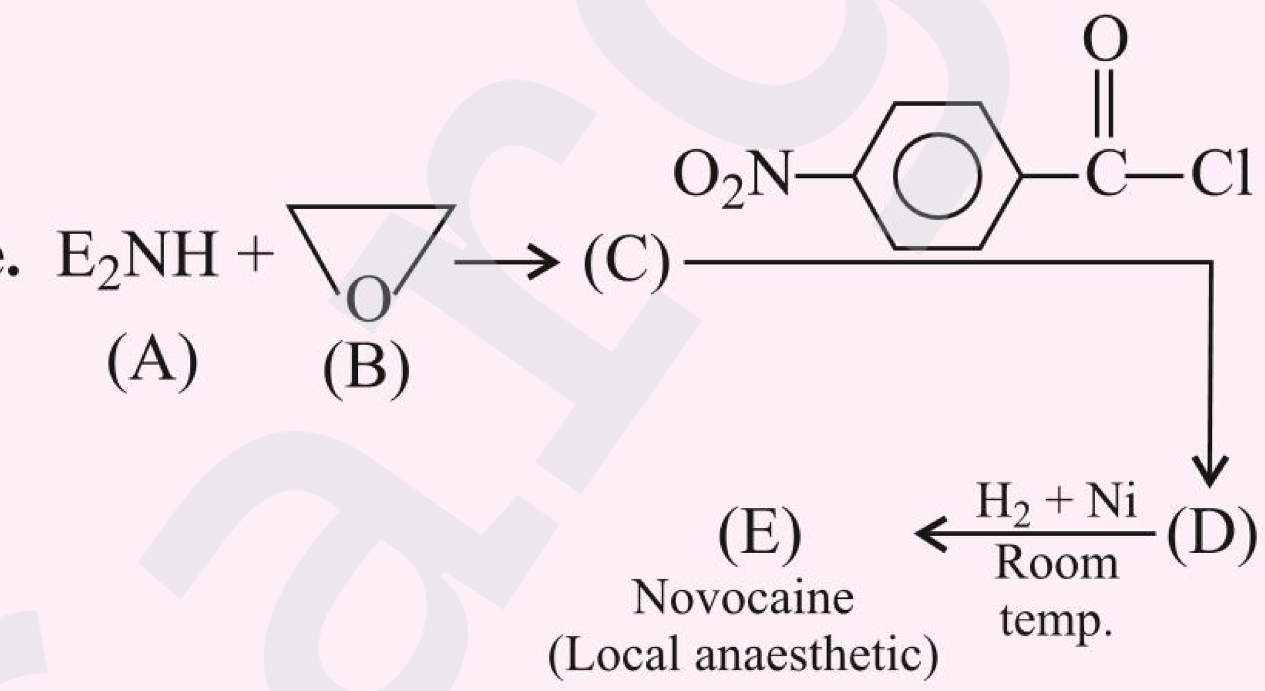
4. Complete the following reactions:

a. $\underset{(A)}{PhNH_2} \xrightarrow[0\text{–}5°C]{HNO_2} (B) \xrightarrow[DH_2PO_2]{} (C)$

b. 

c. $\underset{(A)}{PhCH{=}O} + \underset{(B)}{HCN} \longrightarrow (C) \xrightarrow{LAH} D$

d. $\underset{(A)}{PhCH{=}O} + \underset{(B)}{MeNO_2} \xrightarrow{\overset{\ominus}{O}H} (C) \xrightarrow[H^{\oplus}]{Fe,\ FeSO_4} D$

e. 

5. Explain the formation of the mixture $PhCH_2CHO$ (I) and PhCOMe (II) when $PhCH(OH)CH_2NH_2$ (A) is treated with HNO_2.

6. a. Distinguish between 1°, 2°, and 3° amines by using succinic anhydride (A).

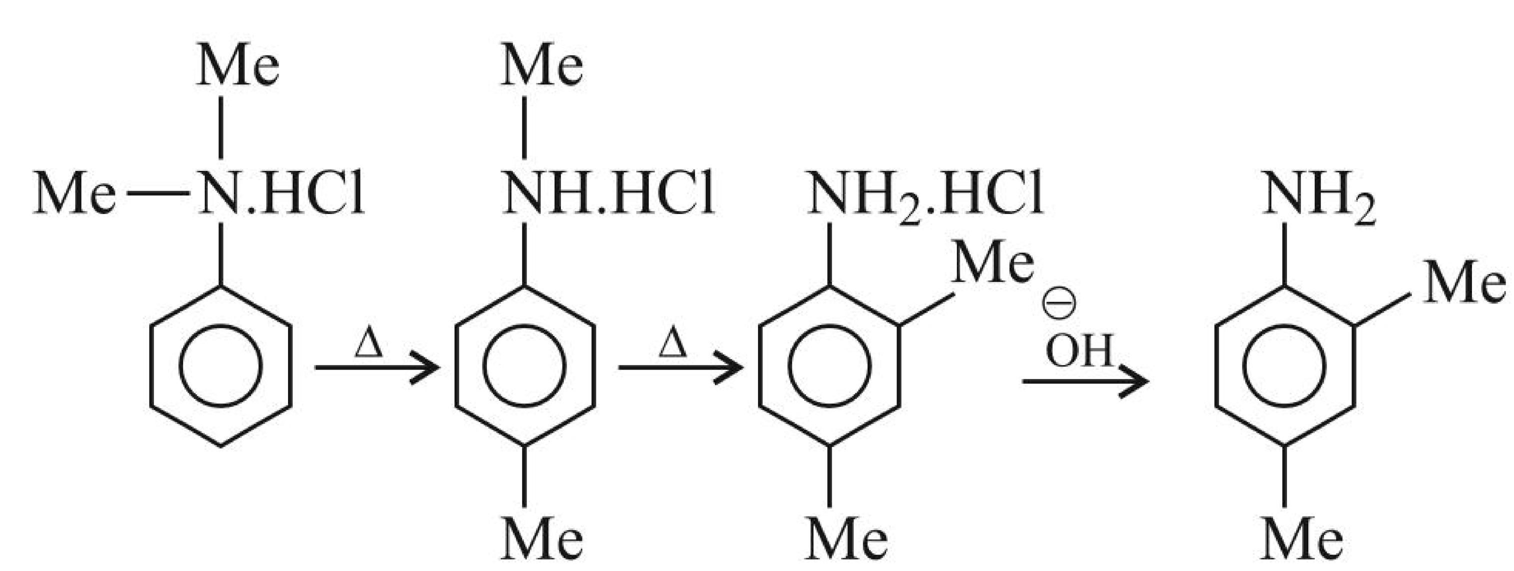
   b. What are the limitations of Hinsberg reagent?

   c. Give the structural formula of a chiral compound $C_8H_{11}N$ (X), which dissolves in dilute HCl and evolves N_2 gas with HNO_2.

7.17 REARRANGEMENT REACTIONS

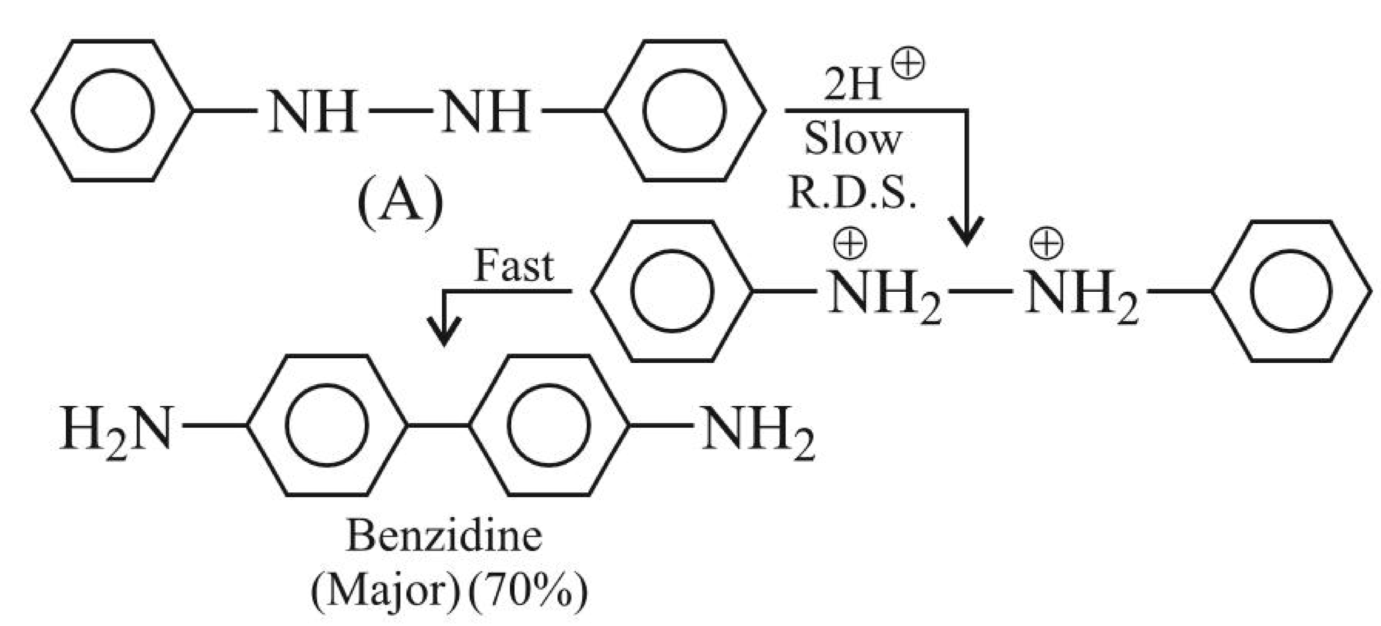
7.17.1 Hofmann–Martius Rearrangement

When a hydrochloride salt of aromatic 3° amine is heated, it undergoes rearrangement reaction in which the alkyl group migrates preferentially to the *p*-position and if it is occupied, then to the *o*-position.



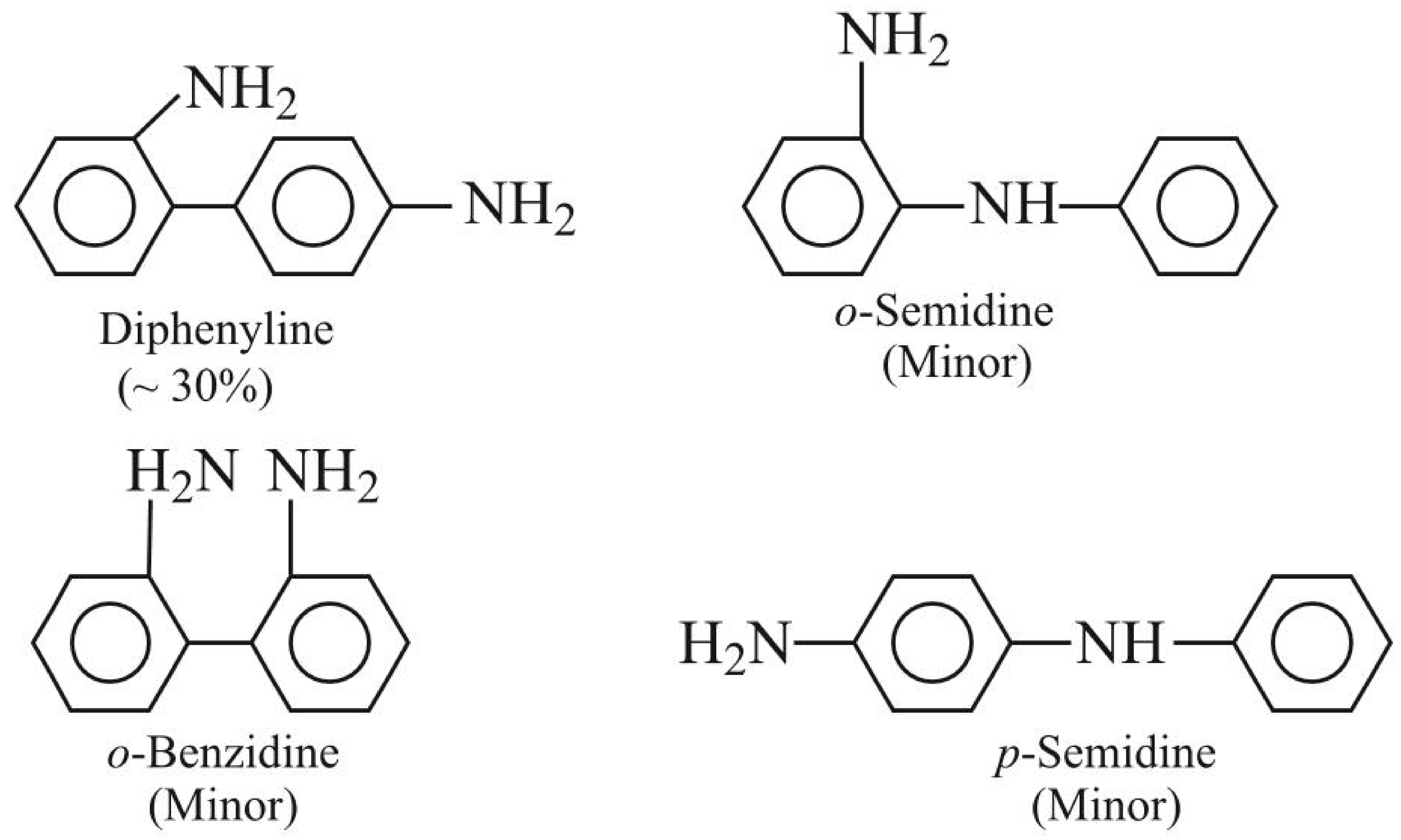
7.17.2 Benzidine Rearrangement Reaction

a. In strongly acidic solution, hydrazobenzene, PhNHNHPh, intramolecularly rearranges to benzidine.

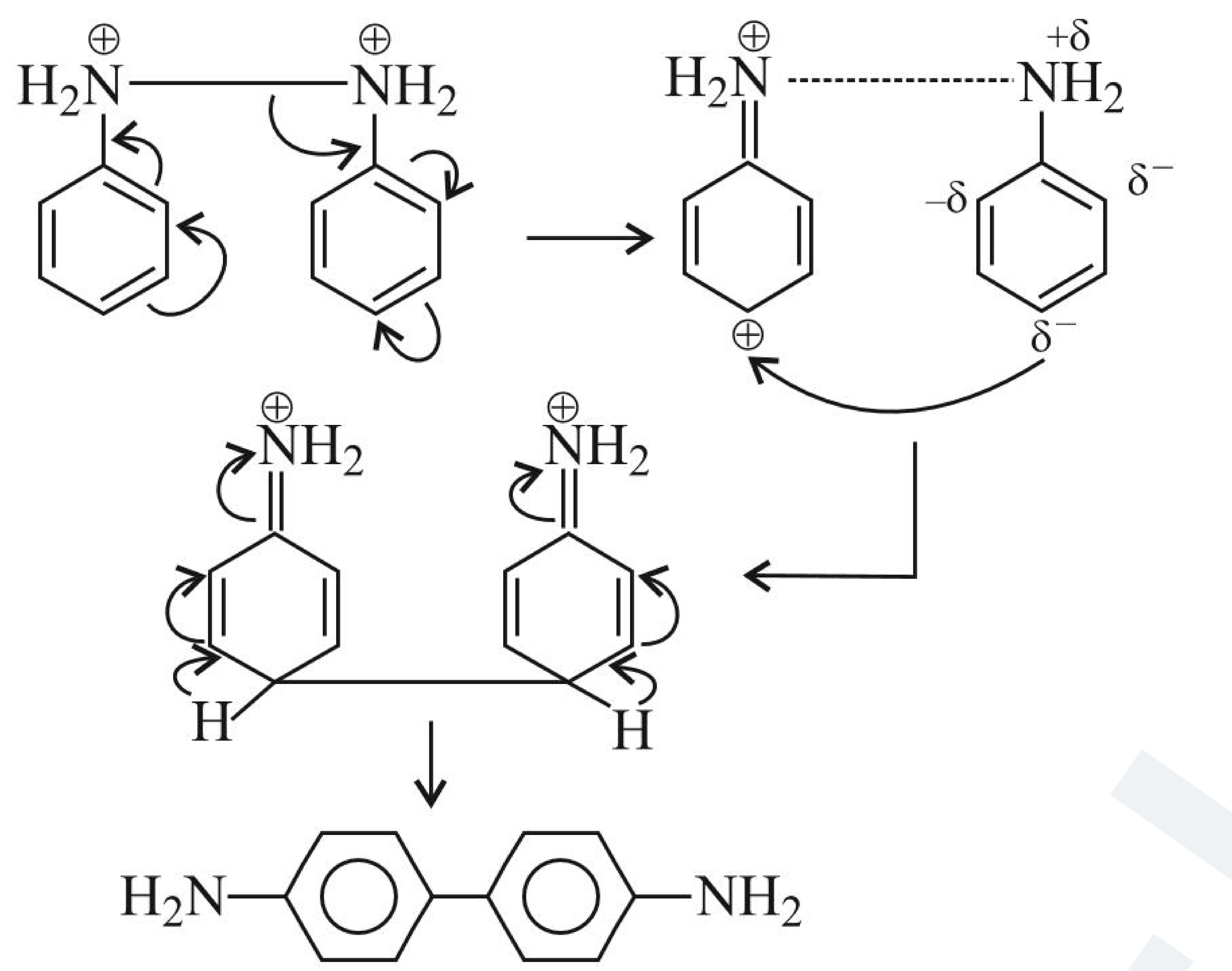


Rate = $K[A][H^{\oplus}]^2$

The other products formed are:



b. Mechanism: The two independent mechanisms can operate in this reaction, a one-proton and a two-proton mechanism. The latter is described here.



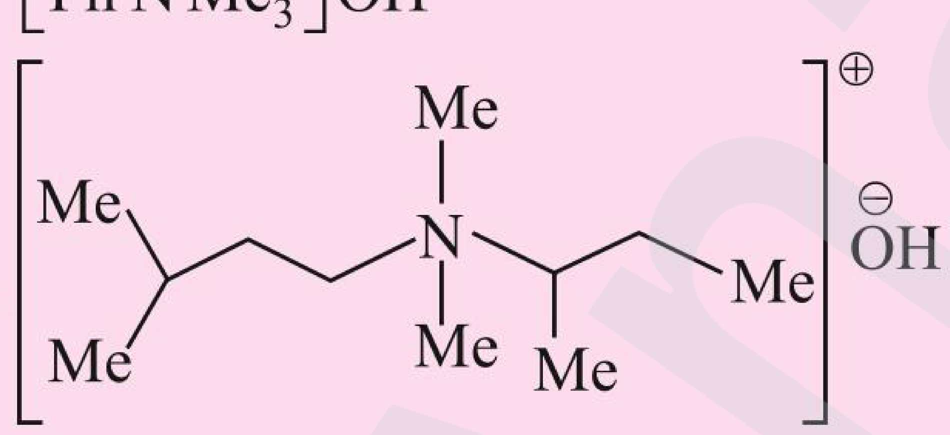
This mechanism leads to C—C linking and can give rise to 4,4′-product (benzidine) and/or to 2,4′-product (diphenyline). Aromatic nuclei lie in approximately parallel planes.

ILLUSTRATION 7.20

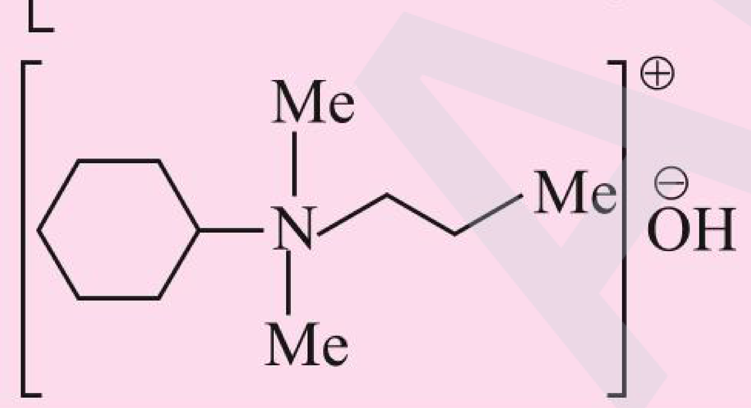
Give the major alkene resulting from the thermal decomposition of hydroxide salt of the following:

a. $\left[Ph\overset{\oplus}{N}Me_3\right]\overset{\ominus}{O}H$

b.

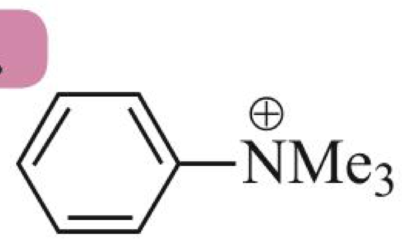


c.



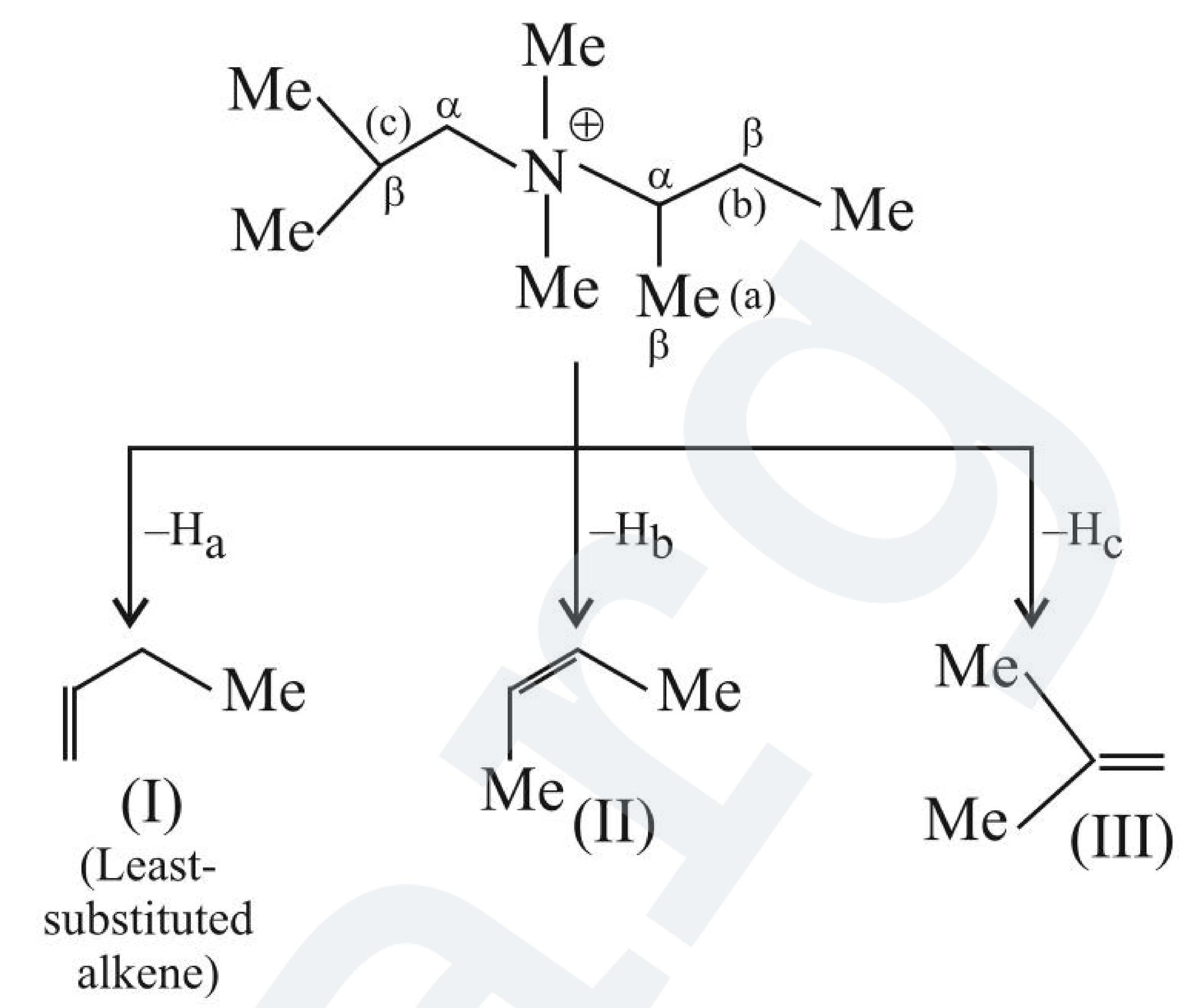
Sol.

a.

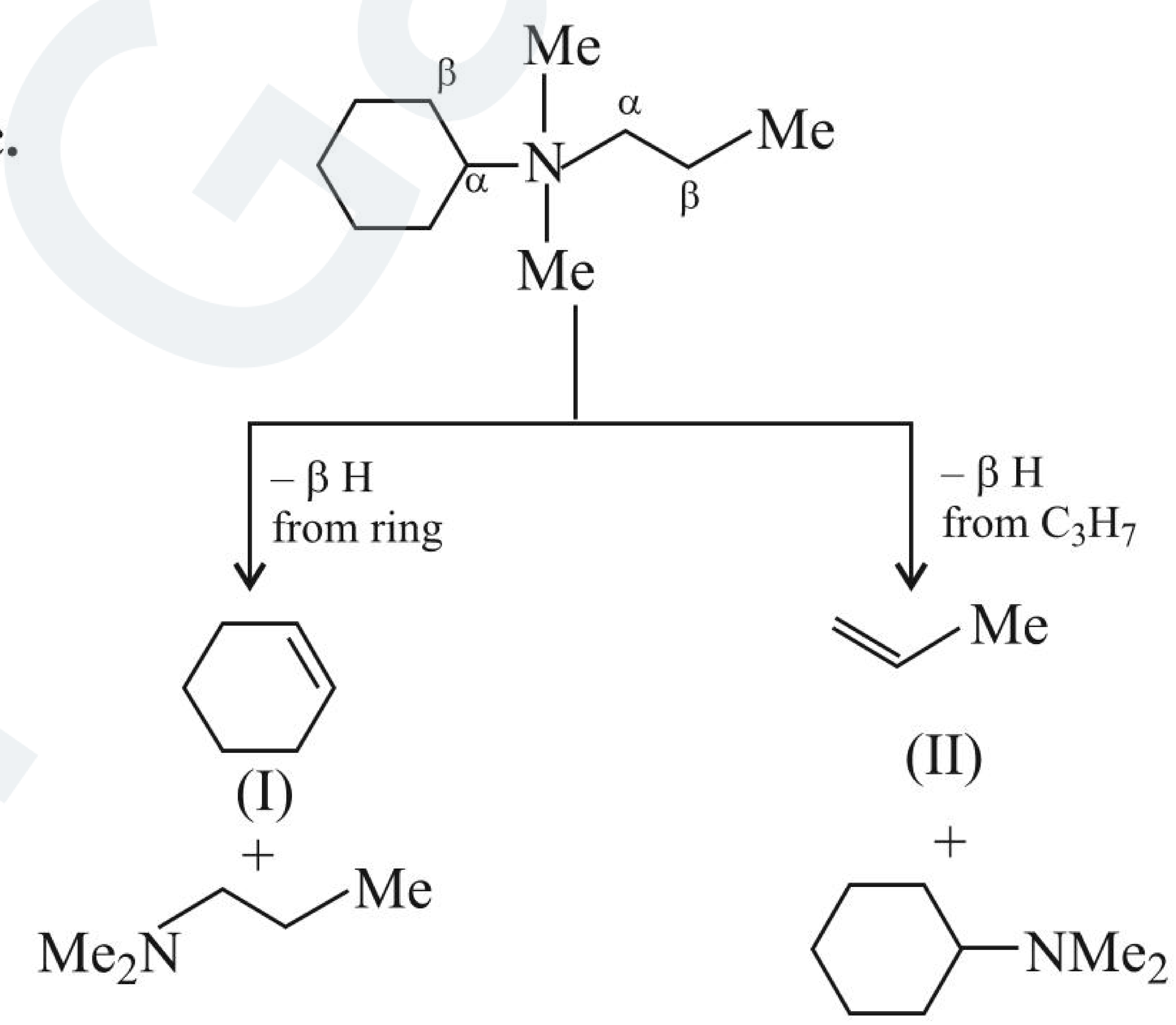


[Compound does not have β-H atom, so base ($\overset{\ominus}{O}H$) displaces one Me group to give MeOH and $PhNMe_2$.]

b. There are three different types of β-H atoms. The major product is obtained by the removal of H_a which gives least-substituted alkene (I).



c.

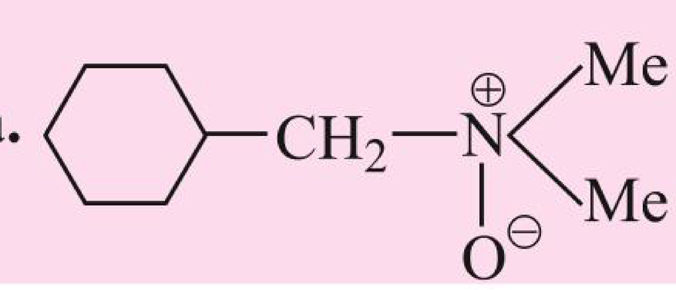


Both the products (I) and (II) are possible.

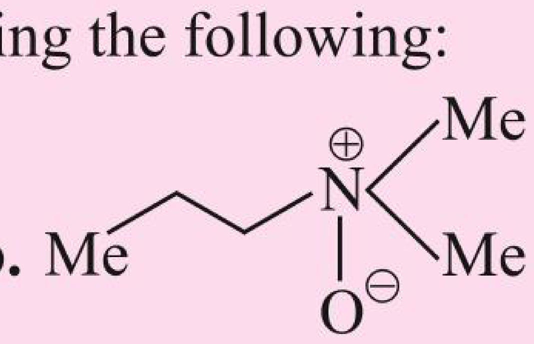
ILLUSTRATION 7.21

Give the product obtained on heating the following:

a.

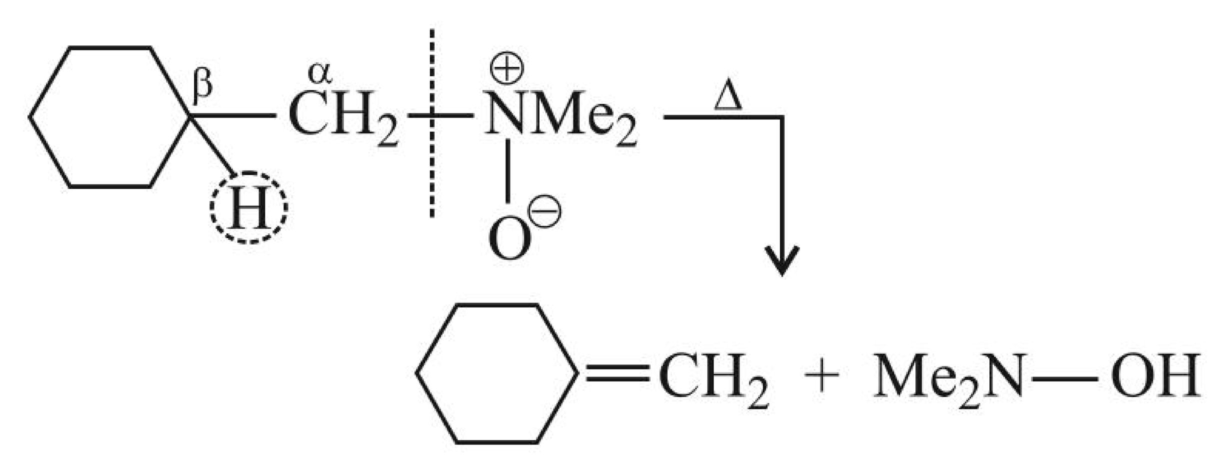


b.



Sol. These are examples of Cope elimination, which gives less-substituted alkene and *N,N*-dialkylhydroxyl amine.

a.



b.

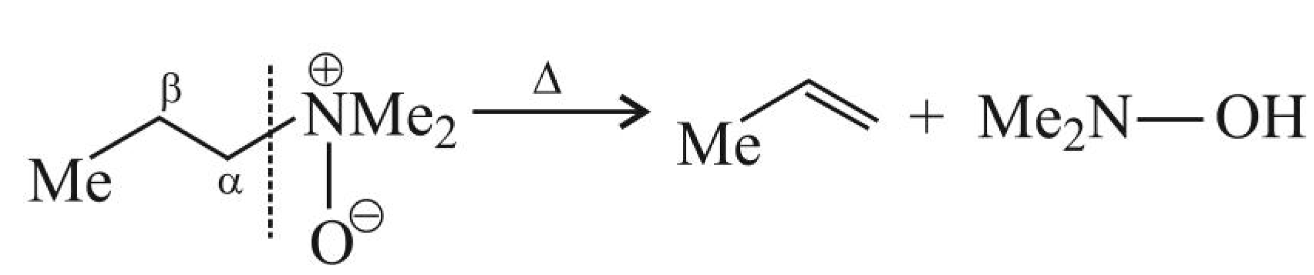
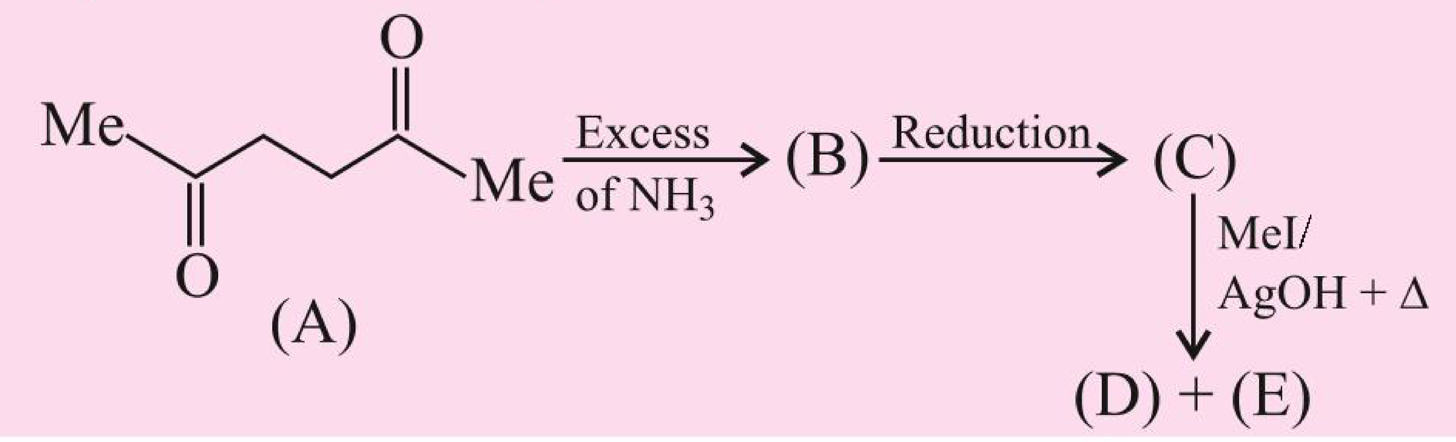
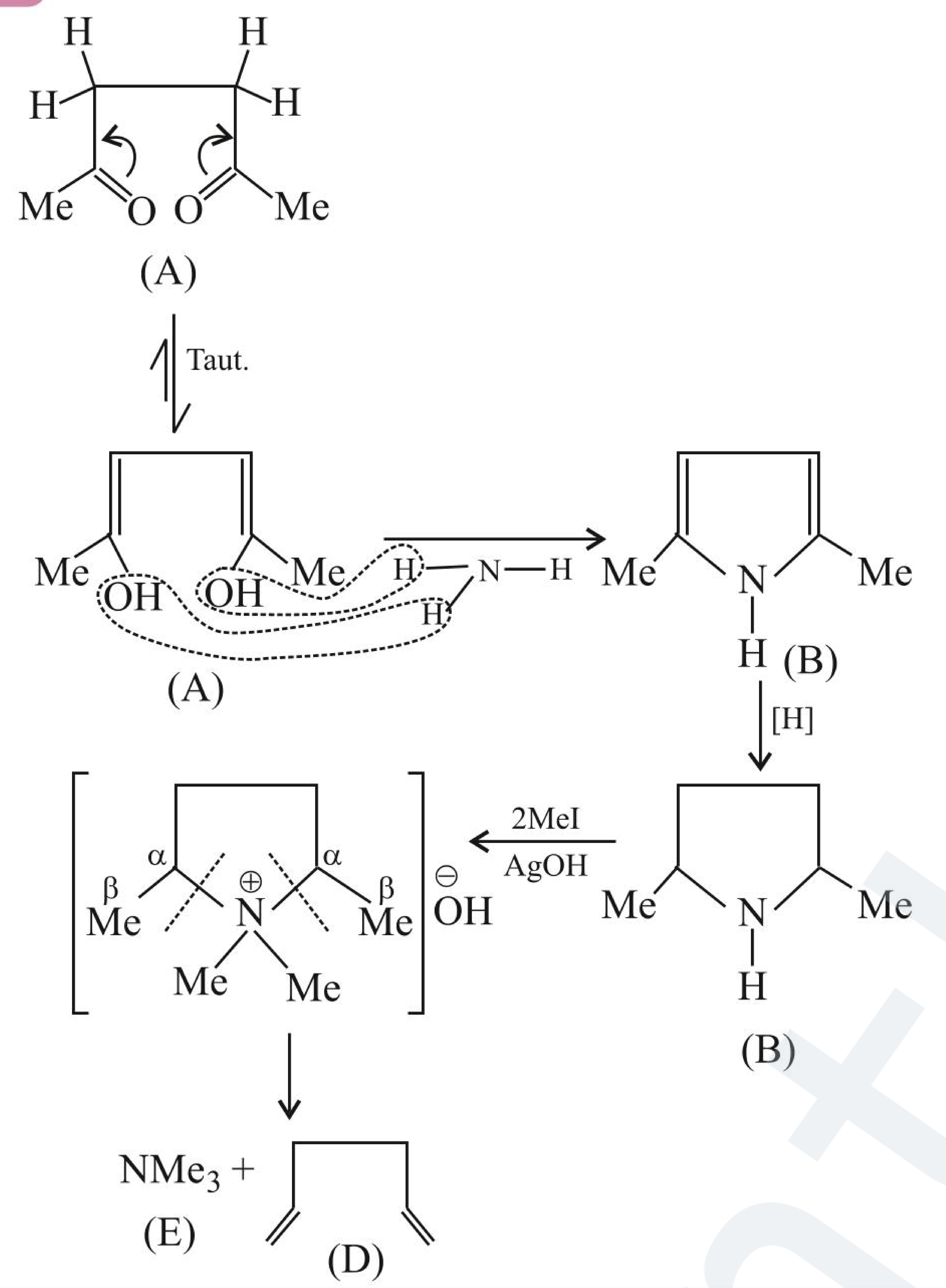


ILLUSTRATION 7.22

Complete the following:

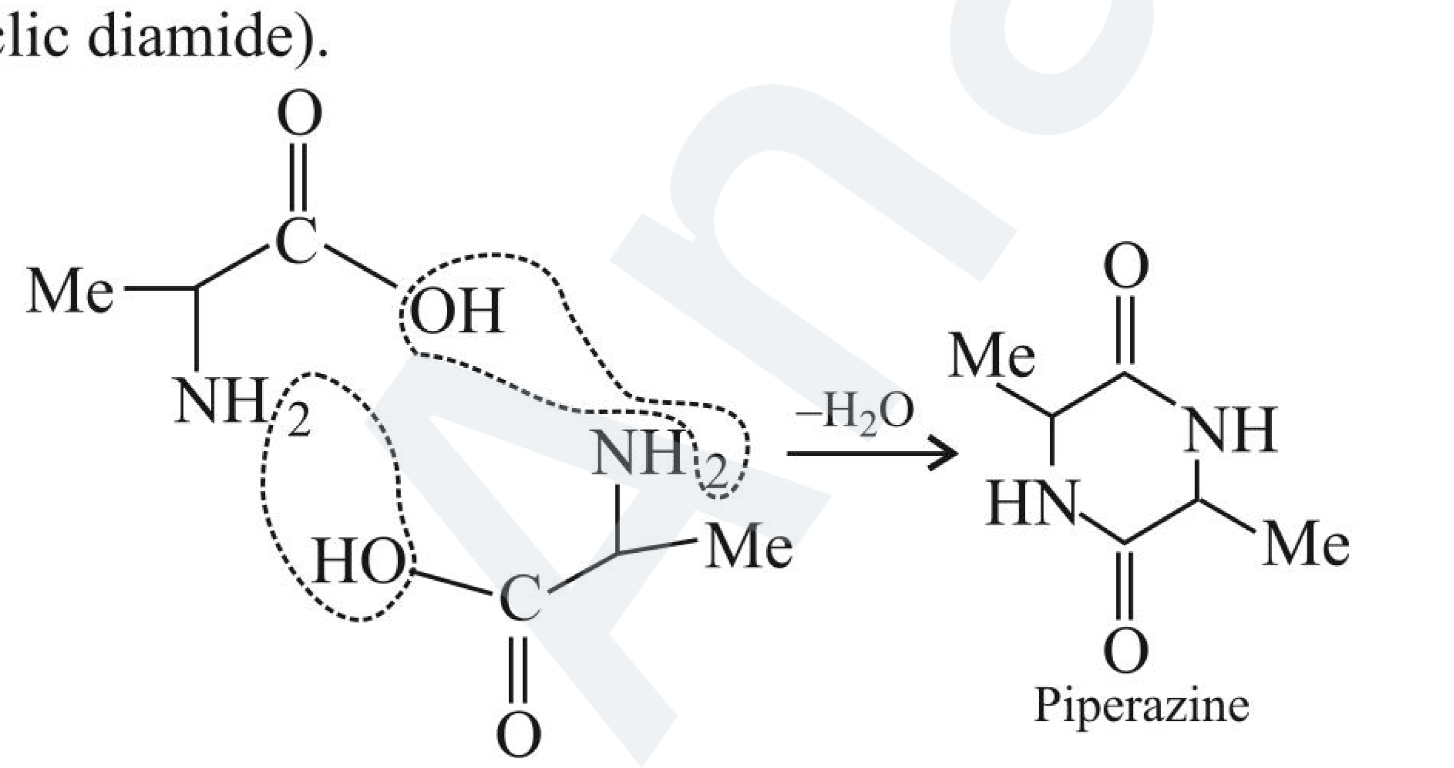


Sol.

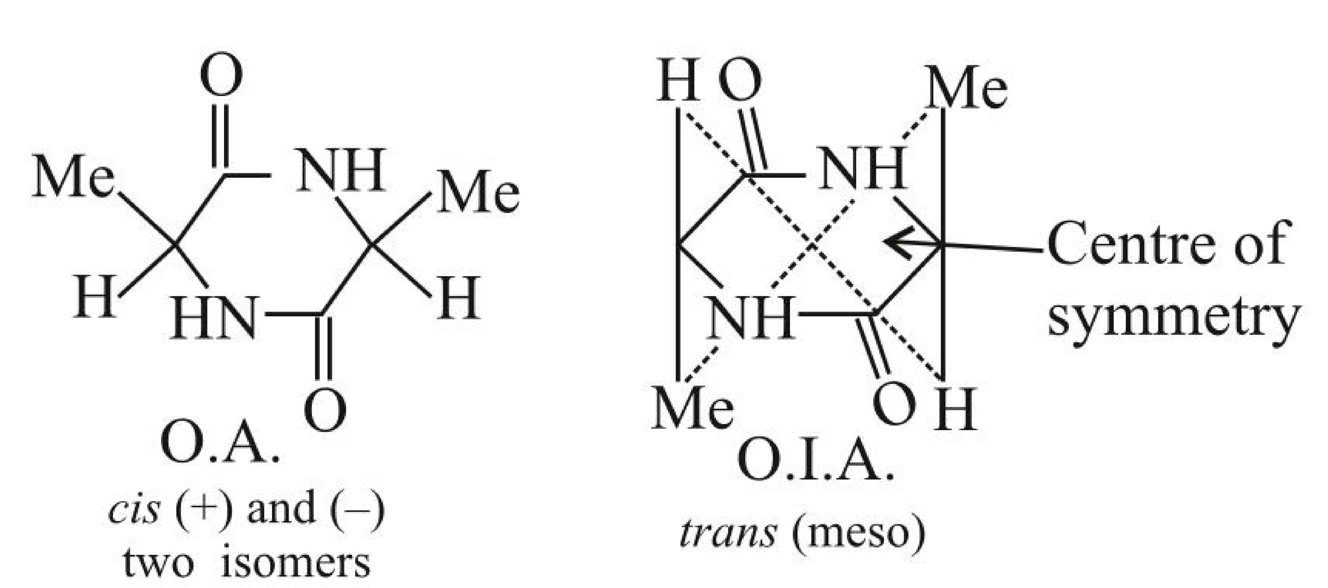


7.18 HEATING OF α-, β-, γ-, δ-, AND ε-AMINO ACIDS

α-Amino acid (like α-hydroxy acid) on heating gives piperazine (cyclic diamide).

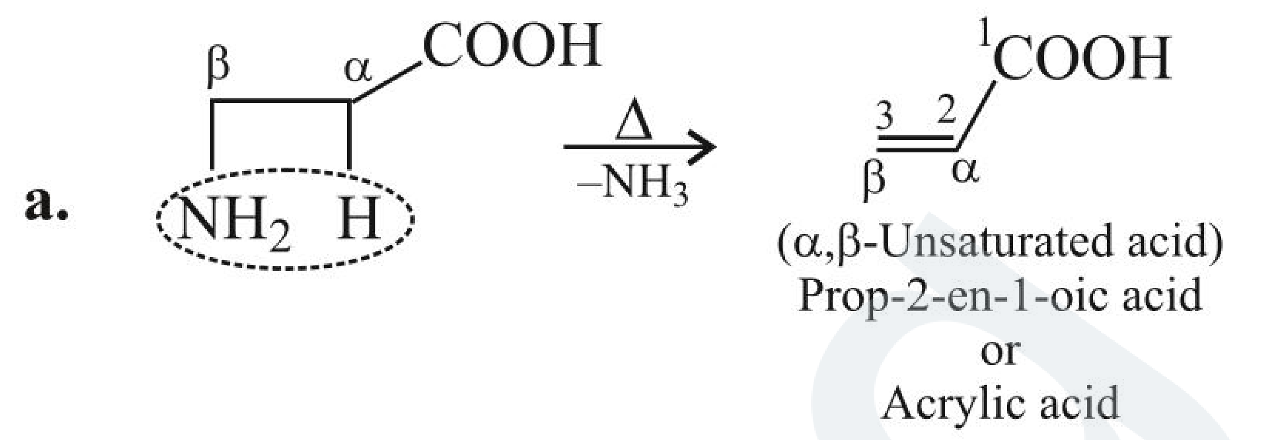


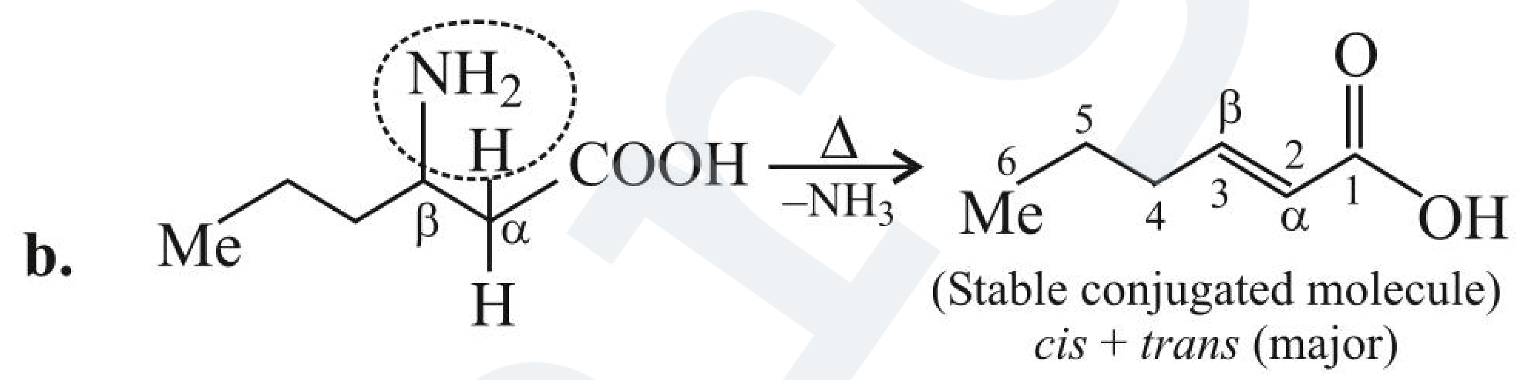
It shows three isomers.



7.18.1 β-AMINO ACID

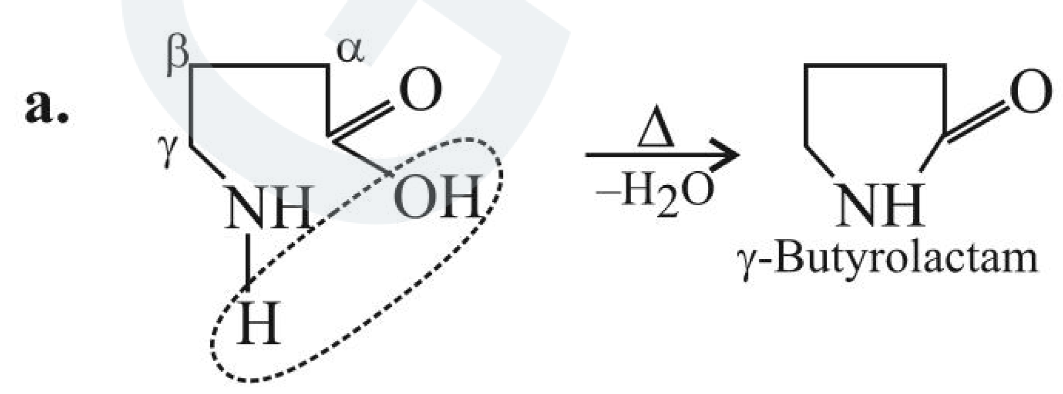
β-Amino acid on heating gives α,β-unsaturated acids (like β-hydroxy acid).

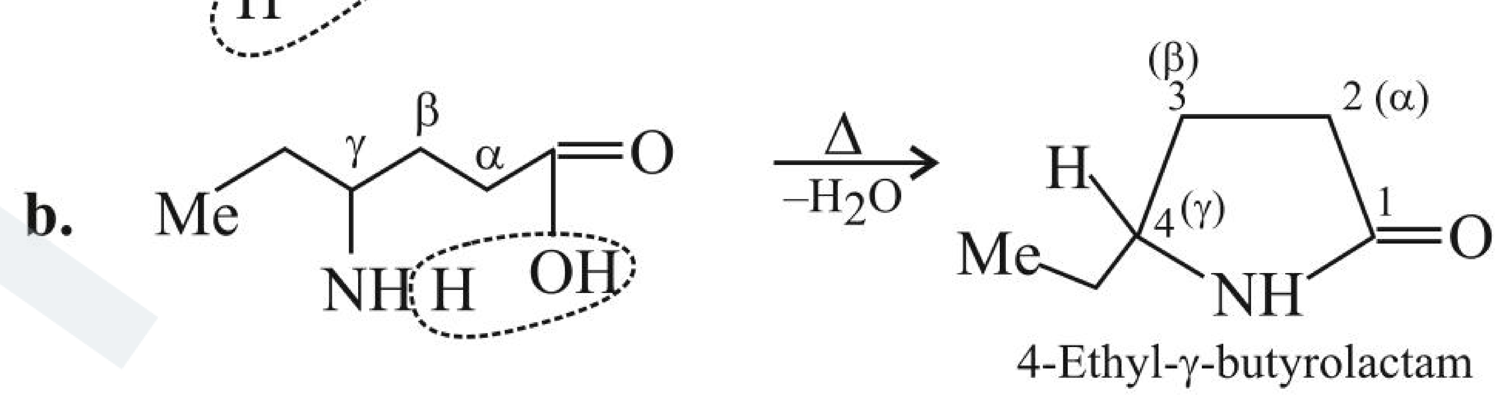




7.18.2 γ-AMINO ACID

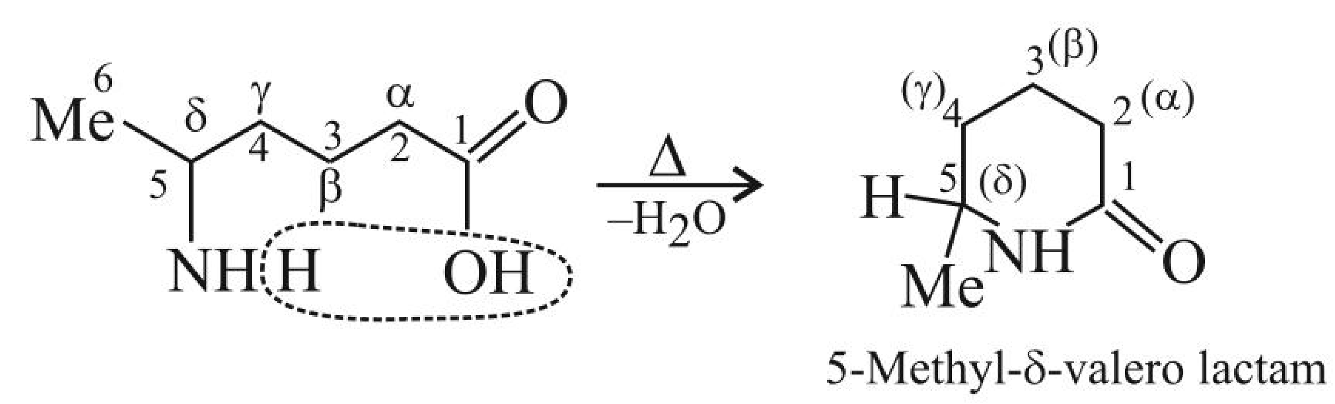
γ-Amino acid on heating gives γ-lactam (cyclic amide) (five-membered cyclic amide) (like γ-hydroxy acids).





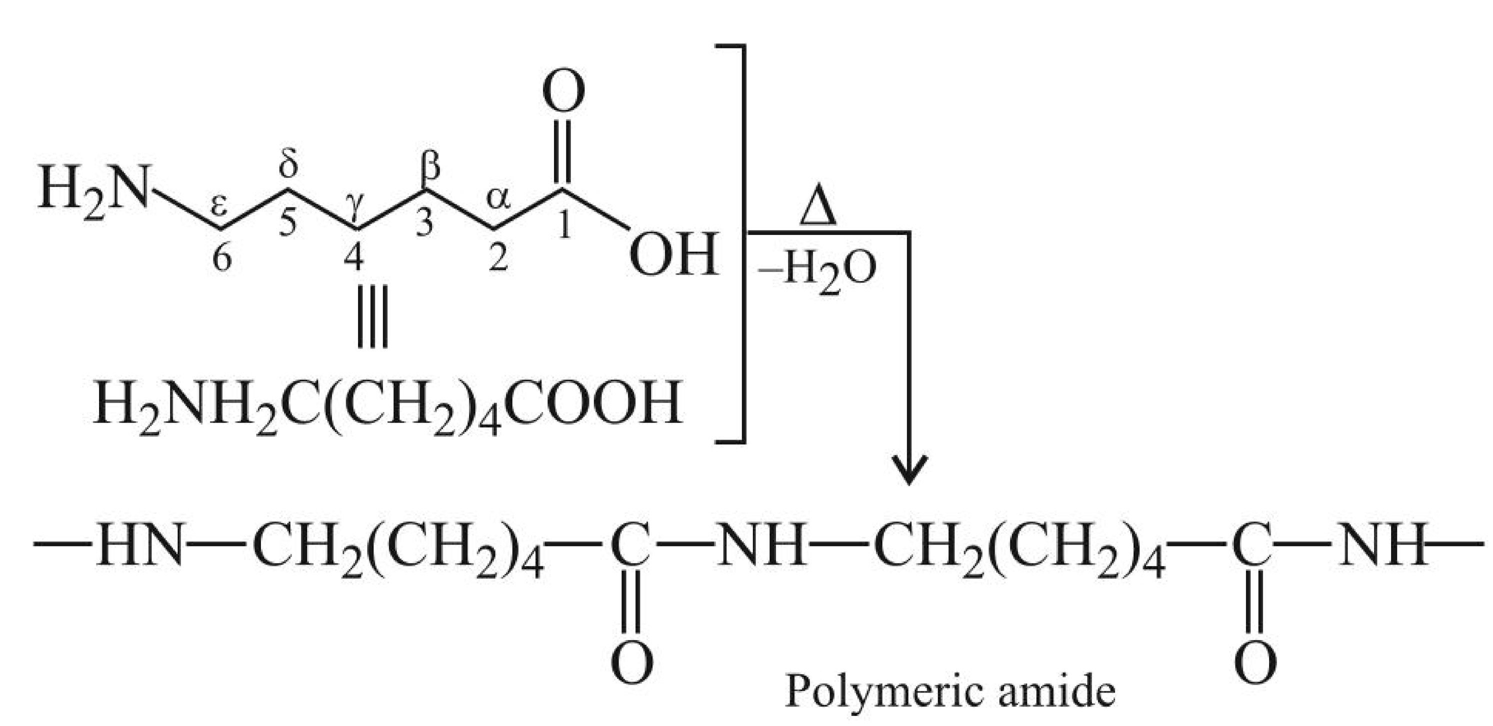
7.18.3 δ-AMINO ACIDS

δ-Amino acids on heating give δ-lactam (cyclic amide) (six-membered cyclic amide) (like δ-hydroxy acid).



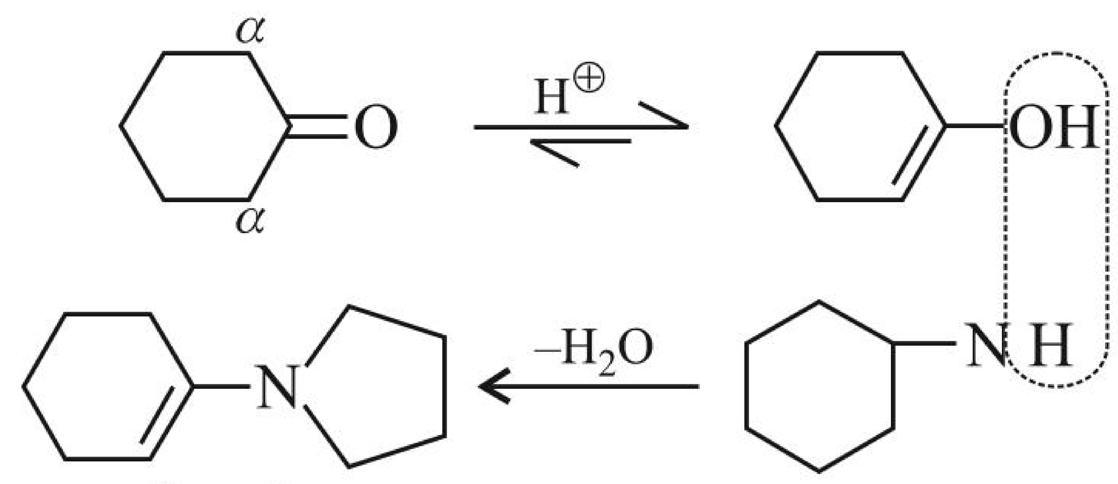
7.18.4 ε-AMINO ACID

ε-Amino acid on heating gives a long-chain polymeric amide (like ε-hydroxy acid) because seven-membered ring is not stable.



Stork Enamine Reaction:

2° Amines react with carbonyl compounds to form enamines. Carbonyl compounds should have at least one α-H-atoms. Enamines are good nucleophiles,



Enamine

7.19 NITRO COMPOUNDS

Both nitroalkanes and nitroarenes are highly polar compounds (dipole moment between 3–4 D) and thus have strong dipole–dipole interactions. As a result, they have much higher boiling points than hydrocarbons of comparable molecular masses. Further, nitroalkanes also have higher boiling points than the less polar isomeric alkyl nitrites.

Nitroalkanes are sparingly soluble in water, while nitroarenes are insoluble. However, both nitroalkanes and nitroarenes are readily soluble in organic solvents.

Most nitroalkanes are quite stable and hence can be distilled without decomposition under atmospheric pressure. In contrast, isomeric alkyl nitrites explode on heating.

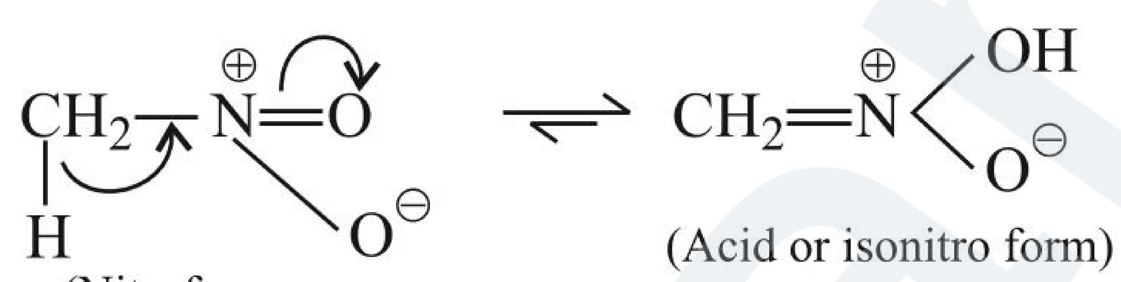
Unlike nitroalkanes, most of the nitroarenes cannot be distilled under atmospheric pressure since they either decompose or explode on strong heating. However, many aromatic nitro compounds (nitrobenzene, *o*-nitrophenol, etc.) are steam volatile and hence can be easily purified.

7.19.1 Reaction of 1°, 2°, and 3° nitroalkanes

Action of 1°, 2°, and 3° nitroalkanes with HONO already discussed in Victor Meyer's method.

7.19.2 Tautomerism

Nitroalkanes containing α-H atoms, i.e., 1° and 2° nitroalkanes, show tautomerism.

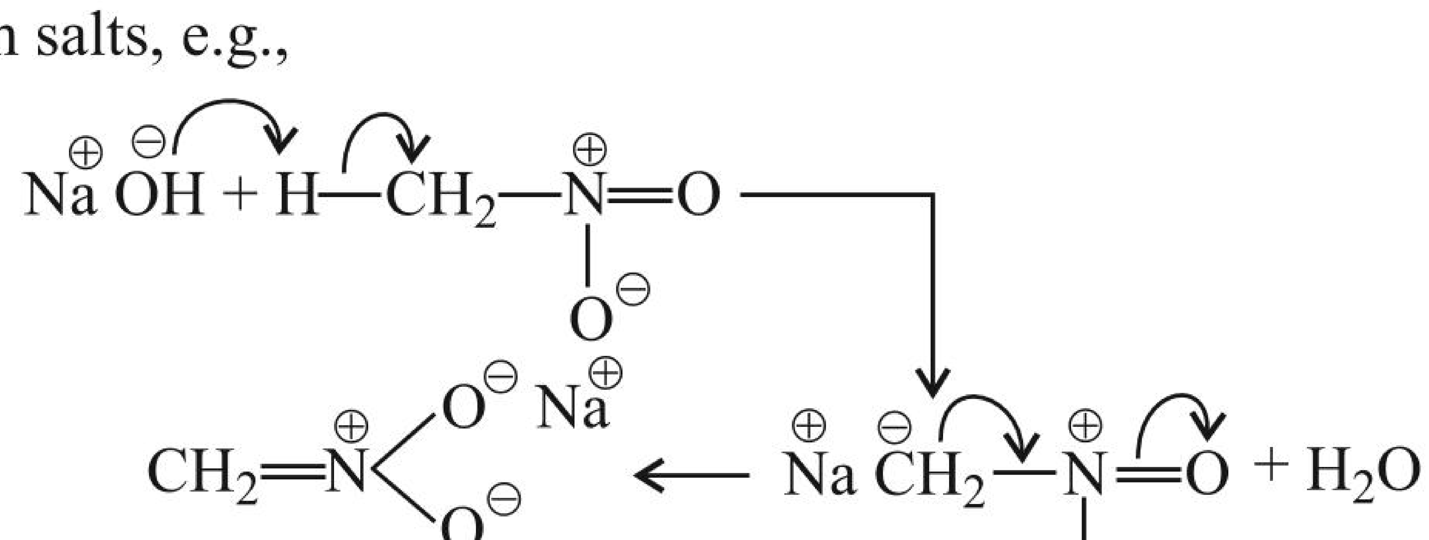


(Nitroform or pseudo acid form) (Acid or isonitro form)

Similarly, nitroethane and 2-nitropropane show tautomerism, while aromatic nitro compounds, i.e., nitrobenzene, *m*-dinitrobenzene, etc., which do not have α-H atoms, do not show tautomerism.

7.19.3 Acidic Character

The α-H atoms of 1° and 2° nitroalkanes are weakly acidic and thus can be abstracted by strong alkalis such as aqueous NaOH. Therefore , 1° and 2° nitroalkanes dissolve in aqueous NaOH to form salts, e.g.,



(I)

The main reasons for the acidic nature of 1° and 2° nitroalkanes are:

i. Strong $\bar{e}$-withdrawing inductive effect of the nitro group.

ii. Resonance stabilisation of the carbonium (I) formed after the removal of proton.

Although 1° and 2° nitroalkanes are weakly acidic, but compared to aldehydes and ketones they are twice as strong acids. For example, pK_a of nitromethane is 10, while that of acetone is 20. Nevertheless, nitroalkanes are neutral to litmus.

7.19.4 Halogenation

1° and 2° nitroalkanes on treatment with a halogen (Cl_2 or Br_2) in the presence of alkali form halonitroalkanes. α-H atoms are successively halogenated, e.g.,

$$CH_3{-}NO_2 + 3Cl_2 + 3NaOH \longrightarrow \underset{\text{Chloropicrin}}{Cl_3C{-}NO_2} + 3NaCl + 3H_2O$$

Chloropicrin is an important insecticide and is also used as tear gas.

7.19.5 SE Reaction

Nitrobenzene on nitration, sulphonation, and halogenation gives *m*-products.

7.19.6 Hydrolysis of Aliphatic Nitro Compounds

i. Primary or secondary aliphatic nitro compounds can be converted to aldehydes or ketones, respectively, by treatment of their carbanion salts with sulphuric acid.

$$R{-}CH_2{-}NO_2 \xrightarrow{\overset{\ominus}{O}H} R{-}\overset{\ominus}{C}H{-}NO_2\overset{\oplus}{M} \xrightarrow{H_2SO_4} RCHO + MNO_3$$

$$R{-}\underset{NO_2}{\underset{|}{C}H}{-}R \xrightarrow{\overset{\ominus}{O}H} R{-}\underset{NO_2}{\underset{|}{\overset{\ominus}{C}}}{-}R\ \overset{\oplus}{M} \xrightarrow{H_2SO_4} R{-}CO{-}R + MNO_3$$

ii. When primary nitro compounds are treated with H_2SO_4 without prior conversion to salts, they give carboxylic acids.

$$RCH_2NO_2 \xrightarrow{H_2SO_4} R{-}\overset{O}{\overset{\|}{C}}{-}NHOH \xrightarrow{H_2O} R{-}\overset{O}{\overset{\|}{C}}{-}OH + NH_2OH$$

iii. 3° nitroalkanes do not generally undergo hydrolysis with HCl.

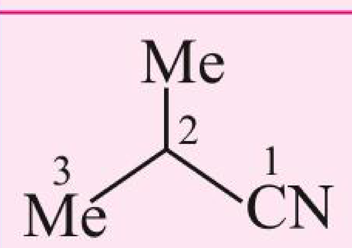
1°, 2°, and 3° nitro compounds are distinguished by HNO_2.

7.20 CYANIDES

Cyanides are a class of compounds which have CN as the functional group and can be regarded as derived from HCN by replacement of H by R/Ar. Unlike HCN and KCN, organic cyanides are much less toxic.

7.20.1 Nomenclature

In the common mode of nomenclature, not used that frequently, the suffix cyanide is added to the alkyl or aryl group. Generally, they are named by replacing the -*ic* or -*oic* (in case of benzoic acid) or -*onic* (in case of propionic acid) from the name of the carboxylic acid with the same number of carbon atoms including the nitrile carbon, by -onitrile. In IUPAC system, suffix nitrile is added to the name of the hydrocarbon atoms. For determining the position of the substituent in a chain, the nitrile carbon is numbered as 1. Some examples of nomenclature using these systems are given below.

S. No.	Compound	IUPAC name	Common name
1.	CH_3CN	Ethanenitrile	Methyl cyanide or Acetonitrile
2.	C_2H_5CN	Propanenitrile	Ethyl cyanide or Propiono-nitrile
3.	$CH_2{=}CHCN$	Prop-2-enenitrile	Vinyl cyanide or Acrylonitrile
4.	Ph—CN	Benzenenitrile	Phenyl cyanide or Benzonitrile
5.		Benzene carbonitrile	Tolylnitrile or *p*-Toluonitrile
6.		2-Methyl propane nitrile	Isopropyl cyanide or Isobutyronitrile

7.20.2 Structure

Organic cyanides possess one sigma and two pi-bonds between C and N atoms and constitute a triple bond as found in alkynes. Thus, nitrogen here is *sp*-hybridised. The (C—C……N) bond angle is 180°. The bond length of the triple bond in (C……N) is shorter than the double bond (C==N) in imines, and (C—N) single bond in amines. The structure of acetonitrile is shown below.

$$\underset{146\text{ pm}}{H_3C—}\overset{116\text{ pm}}{C\equiv N} \quad (180^\circ)$$

7.20.3 Methods of Preparation of Nitriles

The usual way of preparing nitriles is by nucleophilic displacement of the halogen in alkyl/aryl halides and the diazo group in aryl diazonium salts with cyanide from inorganic cyanide. HCN is a source of (—CN) group when added to carbonyl compounds. Primary amides on dehydration are also converted to nitriles.

7.20.4 Nucleophilic Substitution of Alkyl Halides

Aliphatic nitriles are prepared by the treatment of alkyl halides with potassium cyanide in a solvent that will dissolve both the reactants. Since cyanide ion is a strong base, in case of tertiary halides, the elimination is the principal reaction and with secondary halides both the substitution and elimination products are formed.

$$RX + KCN \longrightarrow RCN + KX$$

$$CH_3CH_2Br + CN^{\ominus} \longrightarrow CH_3CH_2CN + Br^{\ominus}$$
(Substitution)

$$(CH_3)_3CBr + CN^{\ominus} \longrightarrow (CH_3)_2C{=}CH_2 + Br + HCN$$
(Elimination)

7.20.5 Substitution of Diazonium Salts

Aromatic nitriles are not formed from unreactive aryl halides but are prepared from aryl diazonium salts through the replacement of diazonium group by CN, by allowing the diazonium salt to react with cuprous cyanide (Sandmeyer's reaction).

$$ArN_2X + CuCN \longrightarrow ArCN + N_2 + CuX$$

7.20.6 Addition of Cyanide Ion to Carbonyl Compounds

They form cyanohydrins with HCN.

7.20.7 Dehydration of Primary Amides

When a primary amide is treated with a strong dehydrating agent such as phosphorous pentoxide, it is converted to the corresponding nitrile. A variety of other dehydrating agents such as thionyl chloride, phosphorous pentachloride, acetic anhydride, etc., can also be used.

1. $RCONH_2 + P_4O_{10} \longrightarrow RCN + \text{Complex phosphates}$

2. $Ph—\underset{\underset{O}{\|}}{C}—NH_2 \xrightarrow[\text{POCl}_3]{\text{SOCl}_2 \text{ or}} Ph—C\equiv N + H_2O$

3. $R—COONH_4 \xrightarrow[\Delta]{P_2O_5} R—CONH_2 \xrightarrow[\Delta]{P_2O_5} RCN + H_2O$

4. $\underset{\text{Aldoxime}}{R—CH{=}N—OH} \xrightarrow[\Delta]{Ac_2O} RCN + H_2O$

7.21 PHYSICAL PROPERTIES

Nitriles are amongst the most polar organic compounds. The dipole moment of acetonitrile is 3.4 D. Due to high polarity, nitriles have rather higher boiling points, despite lack of hydrogen bonding.

	CH_3CN	C_2H_5CN	C_3H_7CN
b.p.(K)	354.6	370.4	244.7

Nitriles are very weak bases. Although protonated nitrile (conjugate acid) is stabilised by resonance, its resonance structure is a vinyl cation which is not very stable. Despite their feeble basic character, their protonation is important in their acid-catalysed reactions. Due to this weak basic nature, nitriles are very poor hydrogen-bond acceptors. Nevertheless, acetonitrile is miscible with water and propionitrile has low solubility in water. Higher nitriles are insoluble in water.

$$CH_3—C\equiv N + H_3O^{\oplus} \rightleftharpoons CH_3—C\equiv \overset{\oplus}{N}H \longleftrightarrow CH_3—\overset{\oplus}{C}{=}NH + H_2O$$

Acetonitrile is used as a solvent of choice for performing many organic reactions because it is not reactive in mild acidic and basic conditions. Having high polarity, it is capable of dissolving a variety of reactants. It has moderate boiling point and can be

easily removed. It is miscible with water and a number of organic solvents.

7.21.1 Chemical Reactions

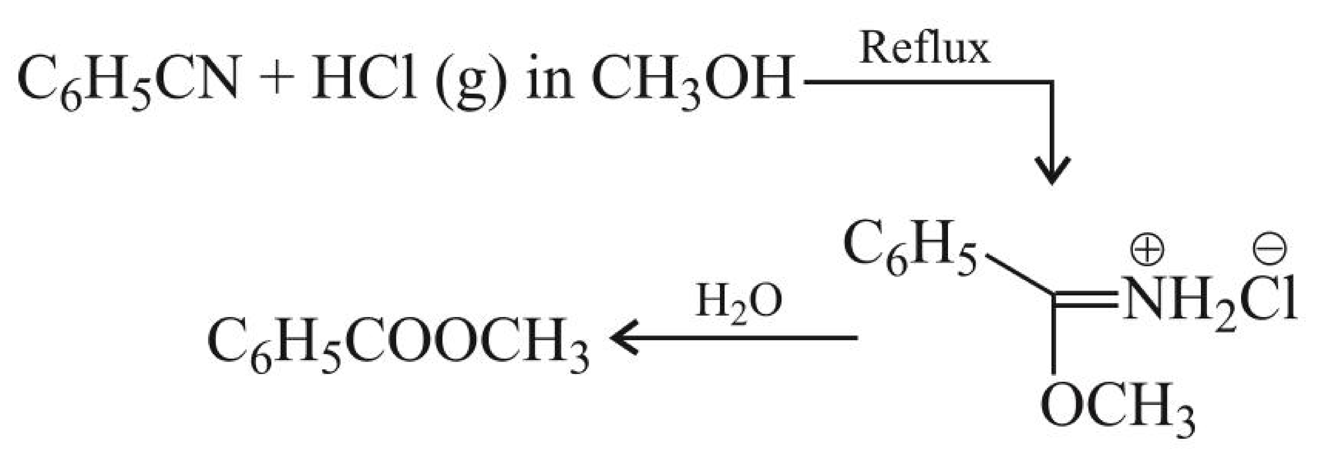
In general, the nitrogen and carbon of the nitrile group can react respectively with an electrophilic and nucleophilic reagent. The unsaturated cyano group can also be reduced. Some important reactions having these types of reactivities are given below.

7.21.2 Hydrolysis

On refluxing with strong aqueous acid or sodium hydroxide solution, nitriles are hydrolysed to carboxylic acids. The intermediate in both the reactions is the primary amide. By using alcohol under acidic conditions, an ester is obtained.

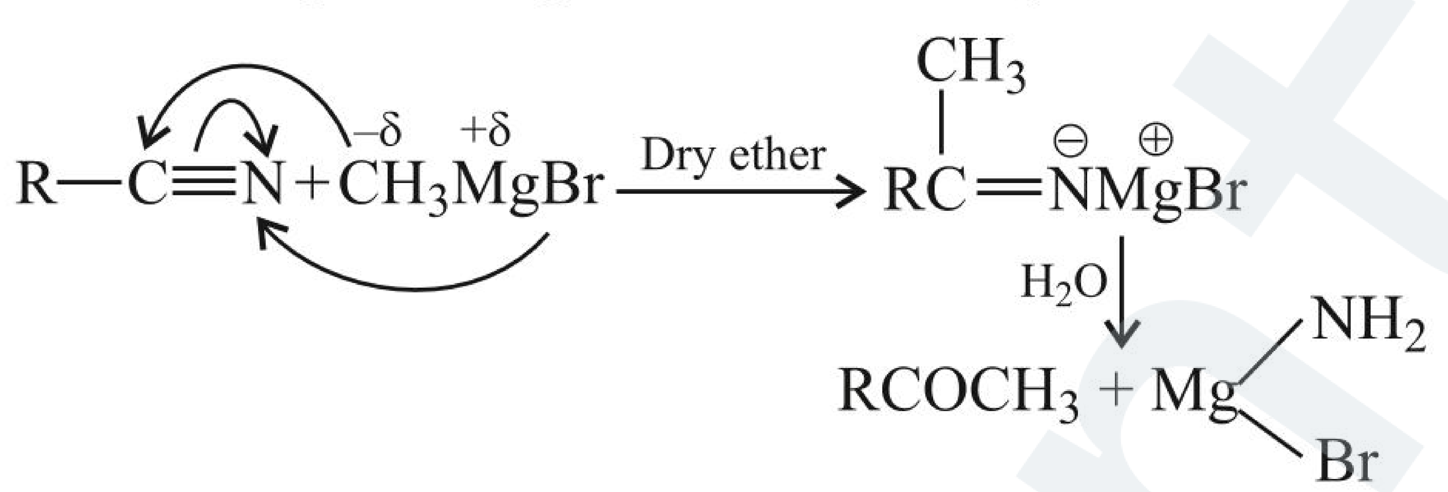
$$C_6H_5CN + 6M\ HCl \xrightarrow{\text{Reflux}} C_6H_5COOH$$

$$C_6H_5CN + 1M\ aq.\ NaOH \xrightarrow[H^+]{\text{Reflux}} C_6H_5COOH$$



7.21.3 Reaction with Grignard reagent

On addition of nucleophilic Grignard reagent, the initially formed imine derivative is hydrolysed to form a ketone. This reaction offers a neat route to obtain ketones as esters which always react further with Grignard reagent to form tertiary alcohols.



7.21.4 Reduction

Nitriles require relatively stronger reagents for reduction. By catalytic hydrogenation in the presence of Raney nickel or on reduction with LAH, nitriles are reduced to primary amines.

$$RCN + LAH \longrightarrow RCH_2NH_2$$

$$RCN + H_2\ (\text{Raney Ni}) \xrightarrow{\Delta} RCH_2NH_2$$

7.22 ISOCYANIDES

7.22.1 Introduction

They are isomeric with cyanides and have (—NC) functional group. The isocyanide group also has a triple bond but constitutes a dipolar species in which nitrogen has a positive charge and carbon has a negative charge ($R—N^{\oplus}\ldots\ldots C^{\ominus}$). This is opposite to the characters of carbon and nitrogen in the cyanide group.

7.22.2 Nomenclature

For naming isocyanides, the word *iso* is prefixed to the name of the corresponding cyano/nitrile compound. Thus, CH_3NC is named methyl isocyanide or acetoisonitrile. In another mode of nomenclature, the suffix carbylamine is added to the name of the alkyl group. Thus, CH_3NC is called methylcarbylamine.

7.22.3 Methods of Preparation

Isocyanides are generally prepared from alkyl halides or primary amines.

1. **From alkyl halides:** When an alkyl halide is heated with silver cyanide, $Ag^{\oplus}$ facilitates the removal of halide ion. A mixture of alkyl isocyanide and alkyl cyanide is formed in which the former is the predominant species. It may be noted that alcoholic KCN gives mainly alkyl cyanide.

$$R—X + AgCN \xrightarrow{\text{Alc. KCN}} RNC + AgX$$

2. **From primary amines:** Both aromatic and aliphatic primary amines on heating with chloroform and aqueous potassium hydroxide form isonitriles.

$$RNH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} RNC + KCl + 3H_2O$$

7.22.4 Chemical Reaction

In an isocyanide, first an electrophile and then a nucleophile add at the carbon to form a species which usually undergoes further transformations:

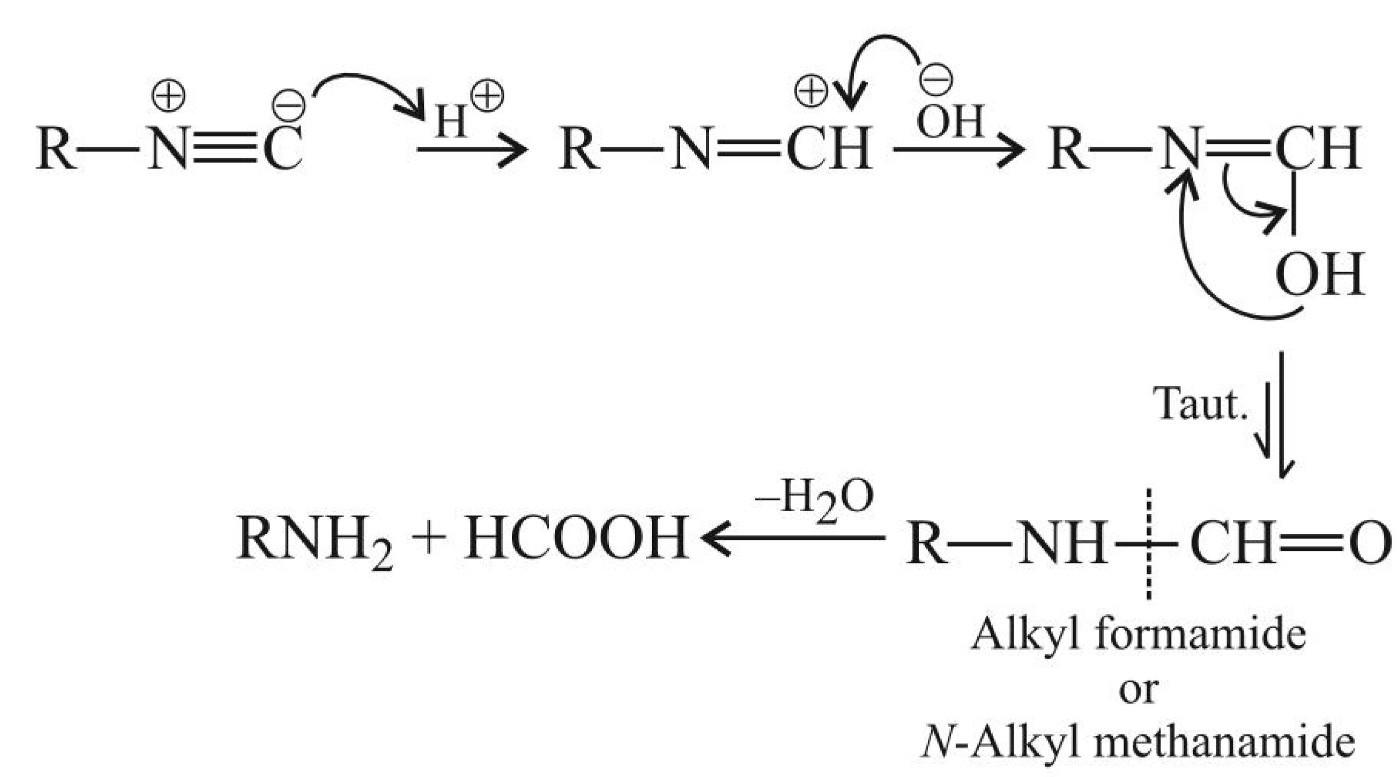
$$R\overset{\oplus}{N}\equiv\overset{\ominus}{C} + \overset{\oplus}{E} \longrightarrow R\overset{\oplus}{N}\equiv CE \xrightarrow{Nu} RN=C(Nu)E$$

Addition of water: Acid-catalysed addition of water gives an N-alkyl formamide derivative.

$$R\overset{\oplus}{N}\equiv\overset{\ominus}{C} + H_2O \longrightarrow RN=CHOH \longrightarrow RNHCHO$$

Mechanism:

First, $H^{\oplus}$ (electrophile) adds at the C atom of $(\overset{\oplus}{N}\equiv\overset{\ominus}{C})$ group and then $\overset{\ominus}{O}H$ (nucleophile) adds on the same C atom.



Note: Ketene ($CH_2=C=O$), cyanide ($R—C\equiv N$), cyanate ($R—N=C=O$), and thiocyanate ($R—N=C=S$) undergo NA (nucleophilic addition) reaction.

Cyanides are hydrolysed with aqueous mineral acids or alkali to give corresponding amides which finally give acids and NH_3.

However, isocyanides are hydrolysed with dilute acids, not by alkali, to first give *N*-alkyl formamide which finally gives corresponding 1° amines and HCOOH.

7.22.5 Reduction with LAH

With LAH as well as on catalytic hydrogenation, isocyanides are reduced to *N*-methylamines.

$$RNC \xrightarrow{LAH} RNHCH_3$$

7.22.6 Oxidation

Isocyanides are oxidised to isocyanates on reaction with HgO or with ozone as well as with a halogen and DMSO (dimethyl sulphoxide).

$$RNC + Cl_2 + CH_3-\overset{\overset{\displaystyle O}{\|}}{S}-CH_3 \rightarrow RNCO + CH_3-\underset{\underset{\displaystyle Cl}{|}}{\overset{\overset{\displaystyle Cl}{|}}{S}}-CH_3$$

7.22.7 Addition Reaction

Isocyanides (but not cyanides) react with halogens, sulphur, mercuric oxide, ozone, etc., to form addition products, e.g.,

i. $CH_3-\overset{\oplus}{N}\equiv\overset{\ominus}{C}: + Cl_2 \longrightarrow \underset{\text{(Methyl imino-carbonyl chloride)}}{CH_3-N{=}CCl_2}$

ii. $CH_3-\overset{\oplus}{N}\equiv\overset{\ominus}{C}: + S \longrightarrow \underset{\text{(Methyl isothiocyantate)}}{CH_3-N{=}C{=}S}$

iii. $C_2H_5-\overset{\oplus}{N}\equiv\overset{\ominus}{C}: + O_3 \longrightarrow C_2H_5-N{=}C{=}O + O_2$

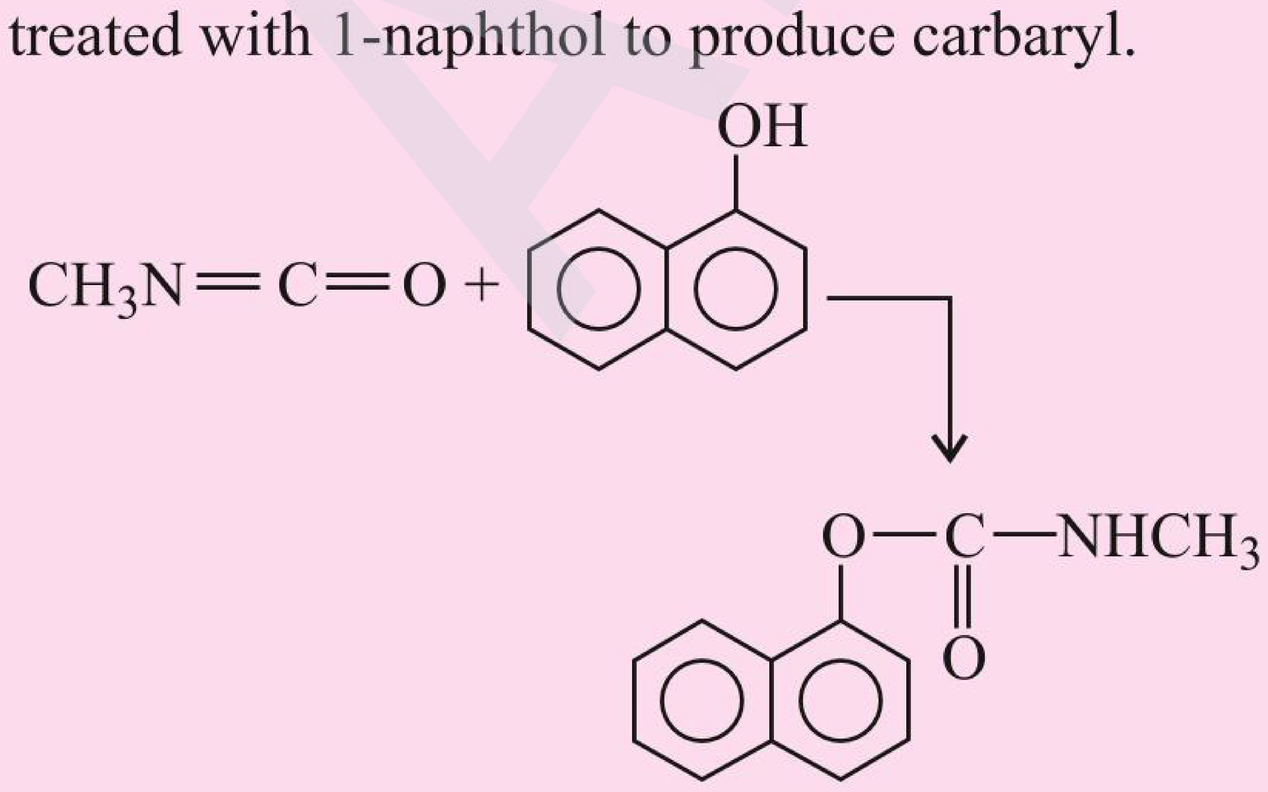
iv. $CH_3-\overset{\oplus}{N}\equiv\overset{\ominus}{C}: + 2HgO \longrightarrow \underset{\text{[Methyl isocyanate (MIC)]}}{CH_3-N{=}C{=}O} + Hg_2O$

MIC gas was responsible for the Bhopal tragedy in December 1984.

BHOPAL GAS TRAGEDY

A major gas tragedy took place on the night of December 2, 1984, when a dense cloud of deadly methyl isocyanate (MIC) gas leaked from a storage tank of the Union Carbide Ltd. plant in Bhopal.

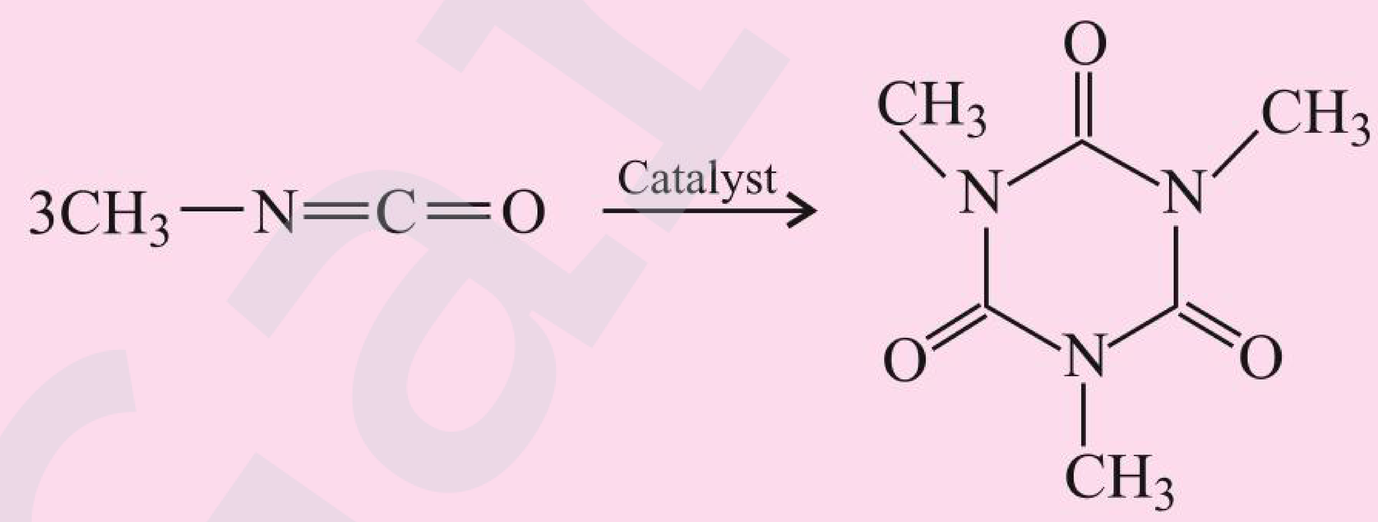
Methyl isocyanate was used to manufacture the insecticide carbaryl, marketed under the commercial name *Sevin*, in this plant. Methyl isocyanate was prepared by the reaction of methylamine (CH_3NH_2) with phosgene ($COCl_2$) [$CH_3NH_2 + COCl_2 \rightarrow CH_3N{=}C{=}O + 2HCl$] and stored in abundance. Subsequently, it was treated with 1-naphthol to produce carbaryl.



There were three tanks in the plant that stored methyl isocyanate. Pressure rose in one of the tanks and blasted its release valve thereby letting methyl isocyanate escape into the atmosphere. What caused the escape of methyl isocyanate gas? A plausible explanation is that possibly a small amount of water seeped into the storage tank and initiated the following hydrolysis reaction.

$$CH_3N{=}C{=}O + H_2O \longrightarrow CH_3NH_2 + CO_2$$

Further, the water that entered the tank was not pure and the impurities present initiated the following polymerisation reaction.

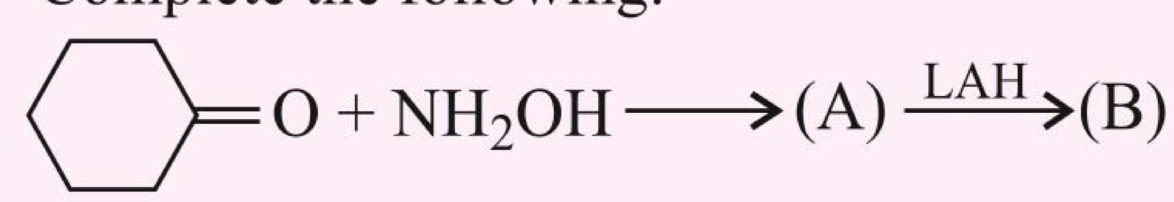


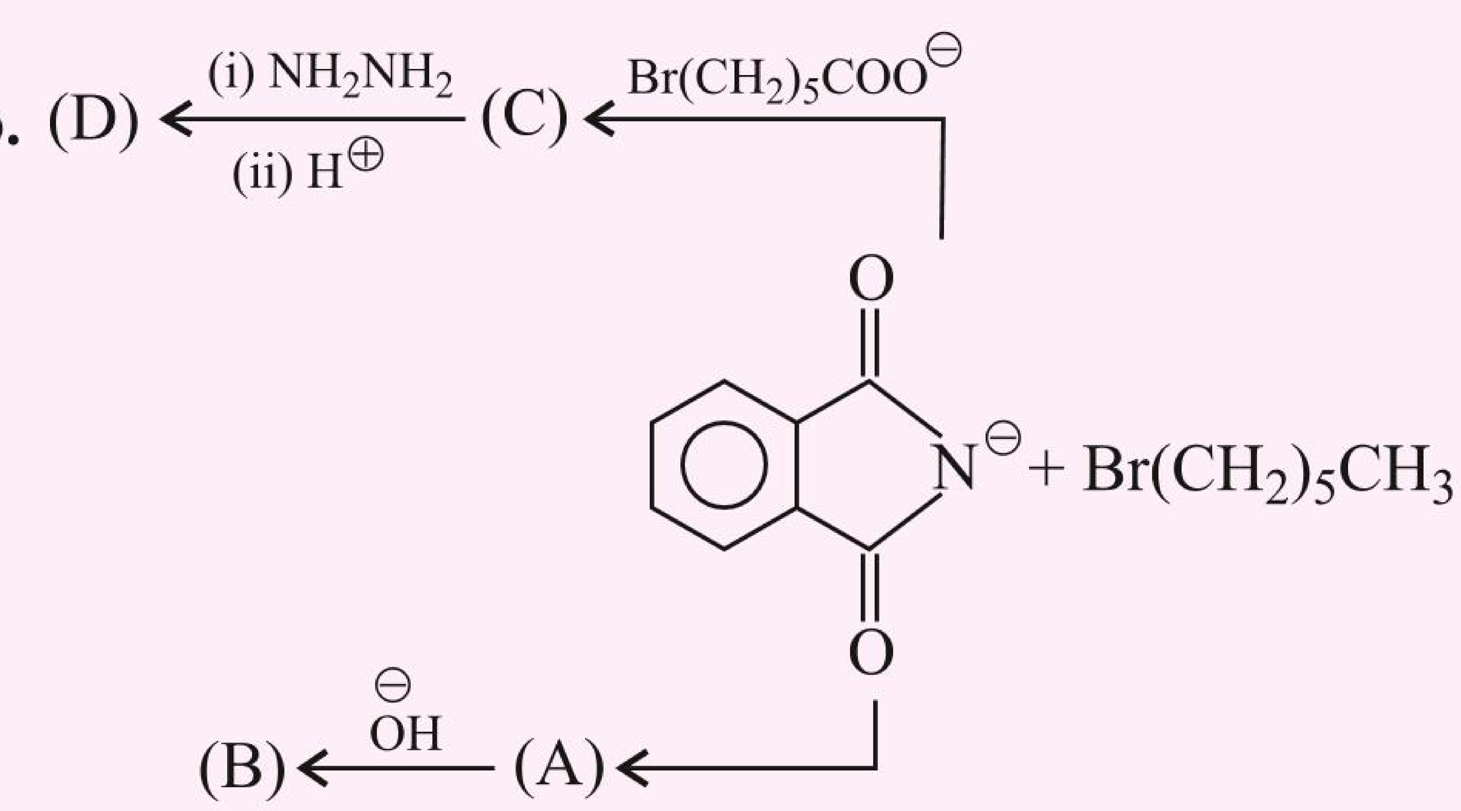
Thus, it was perhaps the simultaneous occurrence of the above two exothermic reactions that led to the escape of the extremely toxic methyl isocyanate gas from the reservoir.

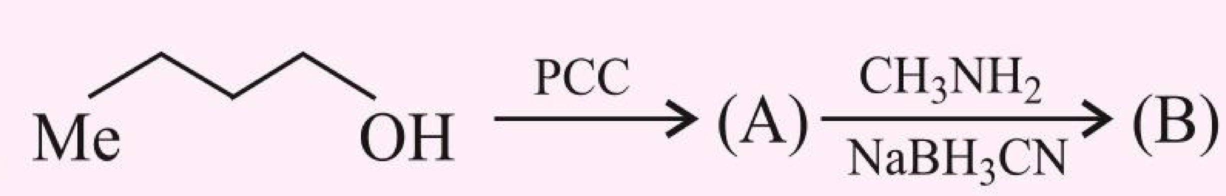
As the cloud of methyl isocyanate rose over the city, it caused an immense loss of life and injury to people and livestock.

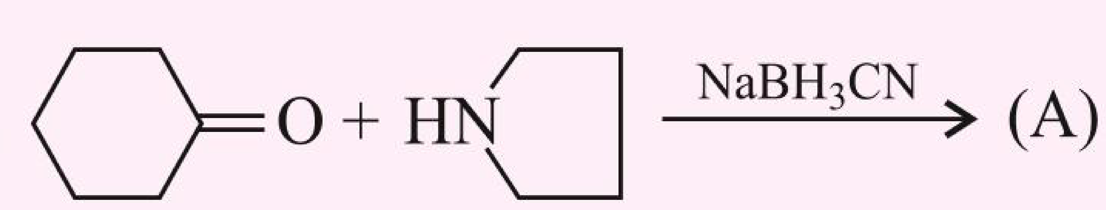
Concept Application Exercise 7.3

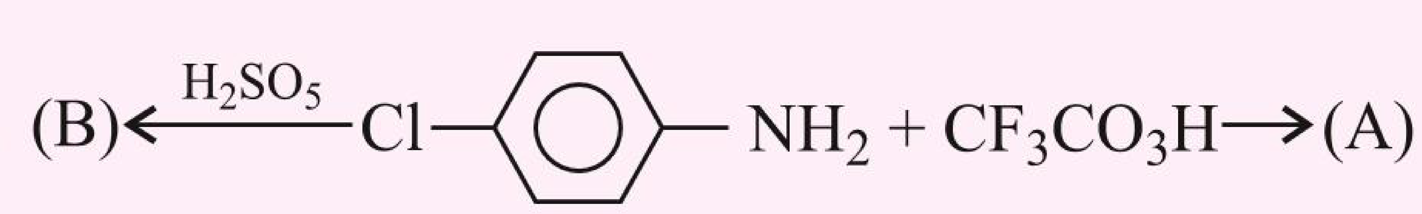
1. Complete the following:

a. 

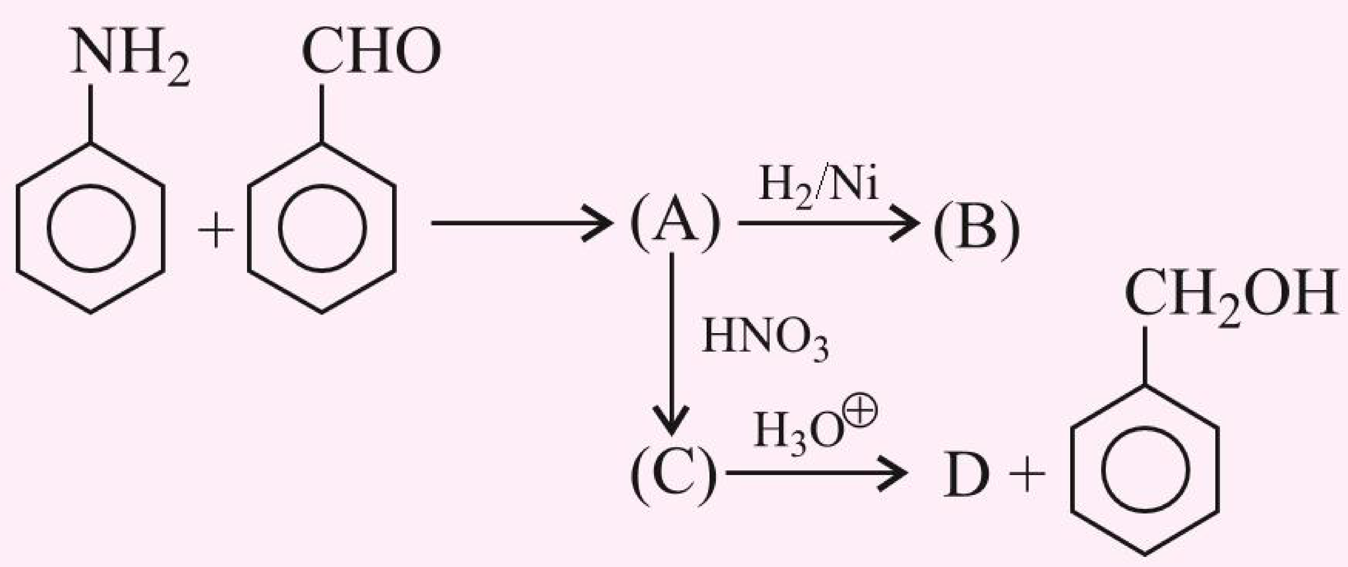
b. 

c. 

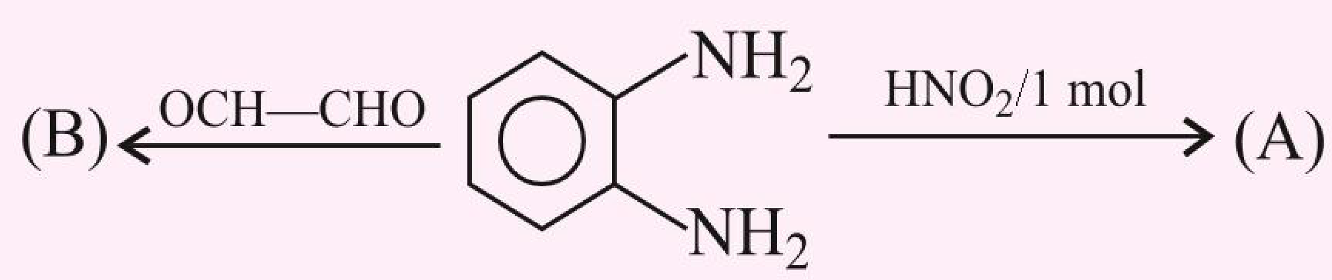
d. 

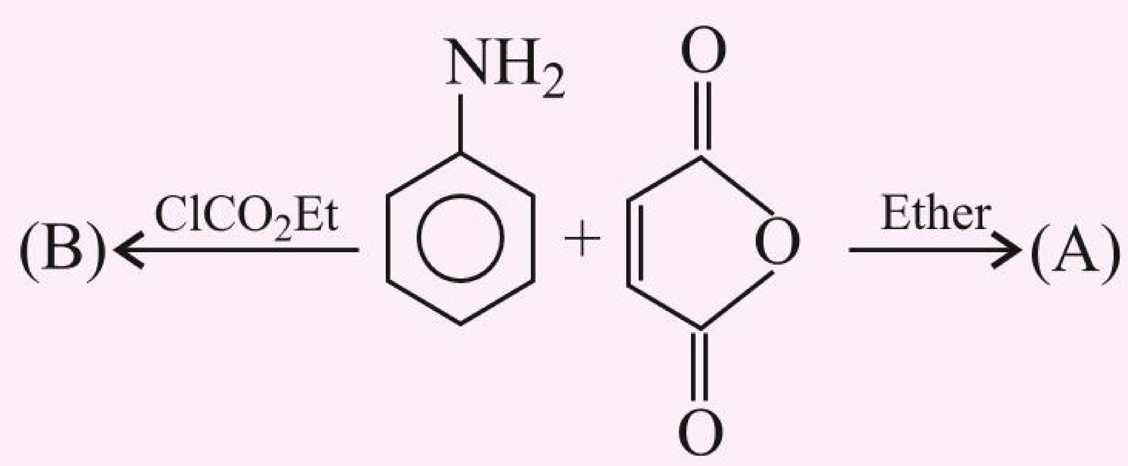
e. 

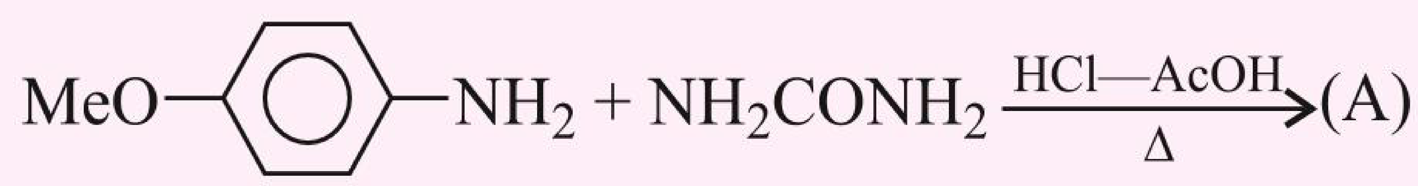
2. Complete the following:

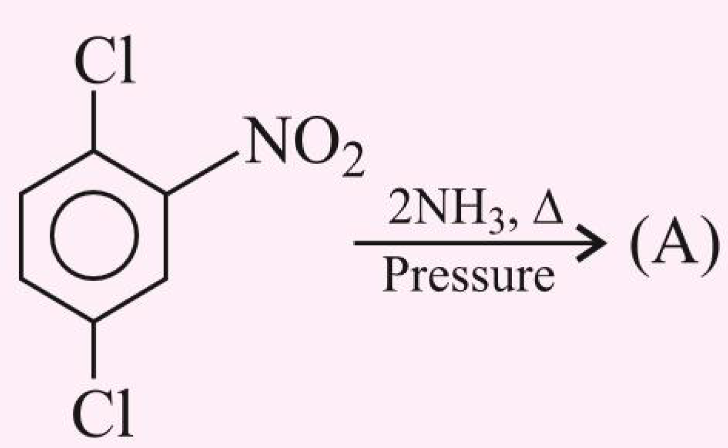


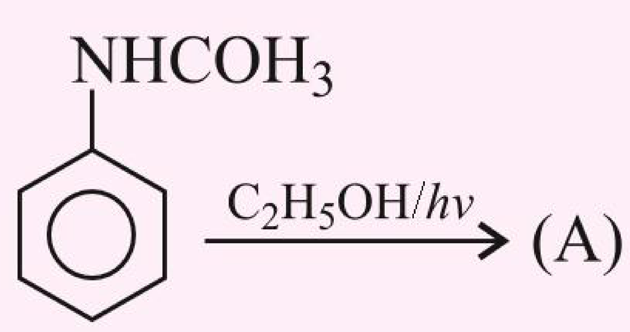
3. Complete the following:

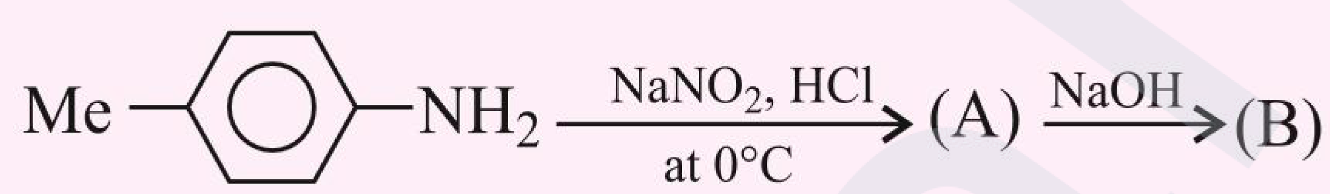
a. 

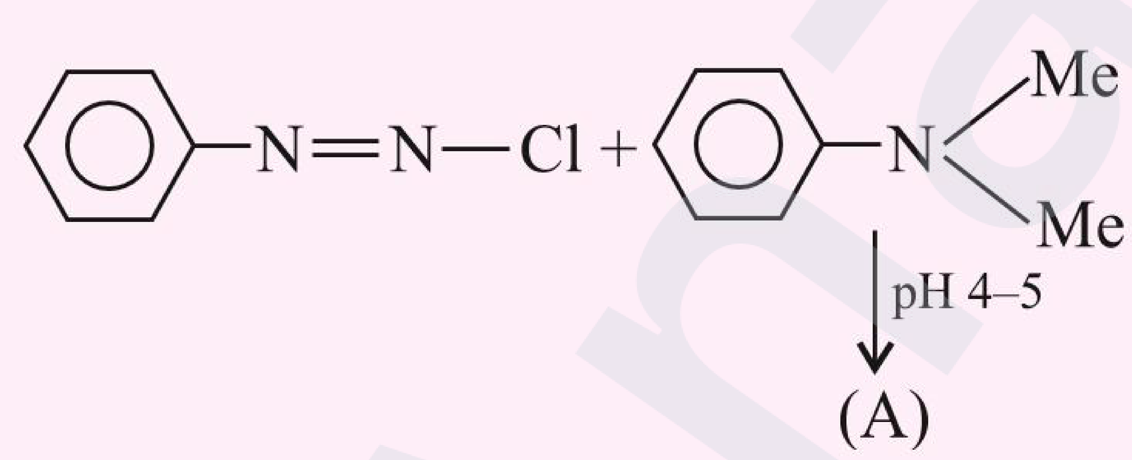
b. 

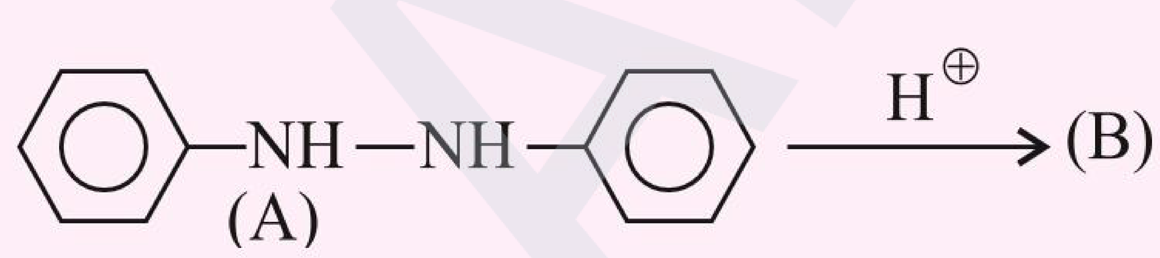
c. 

d. 

e. 

f. 

g. 

h. 

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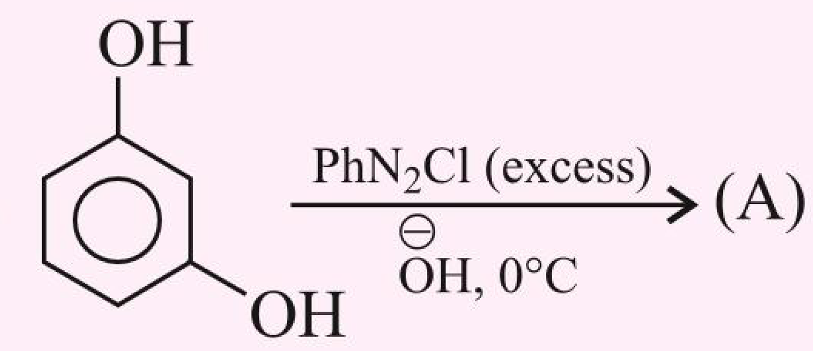
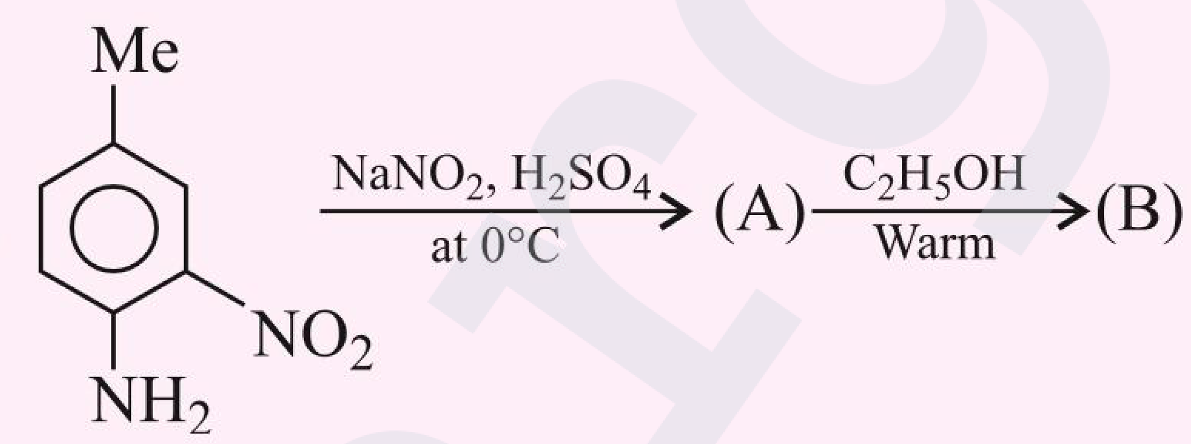
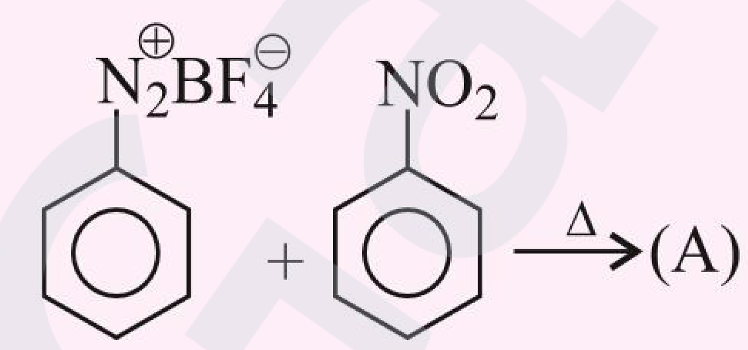
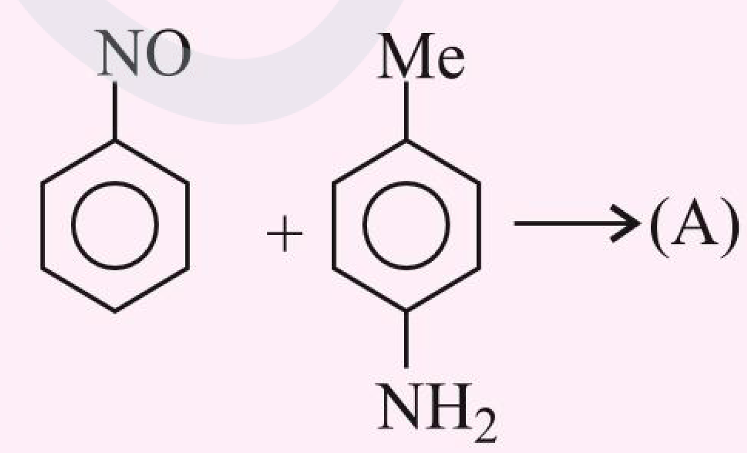
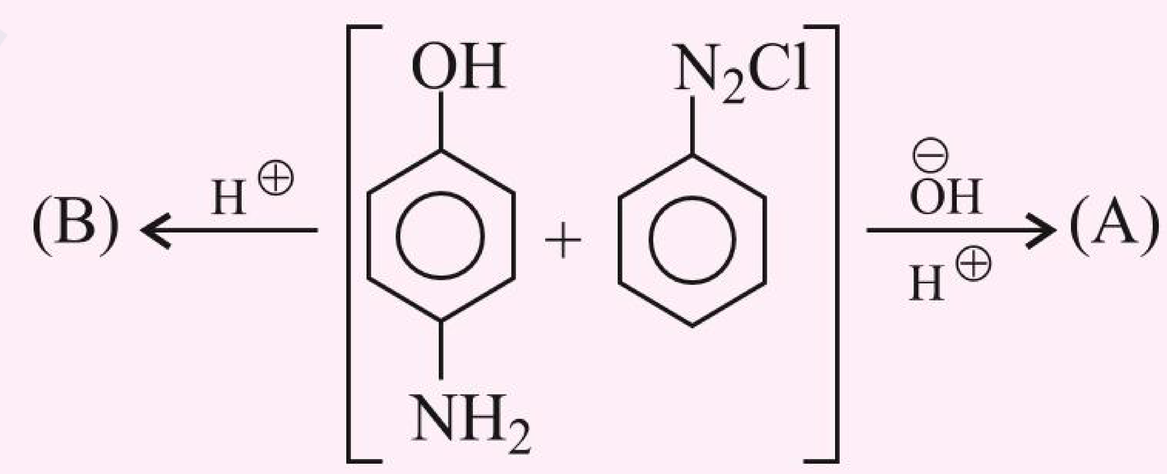
j. 

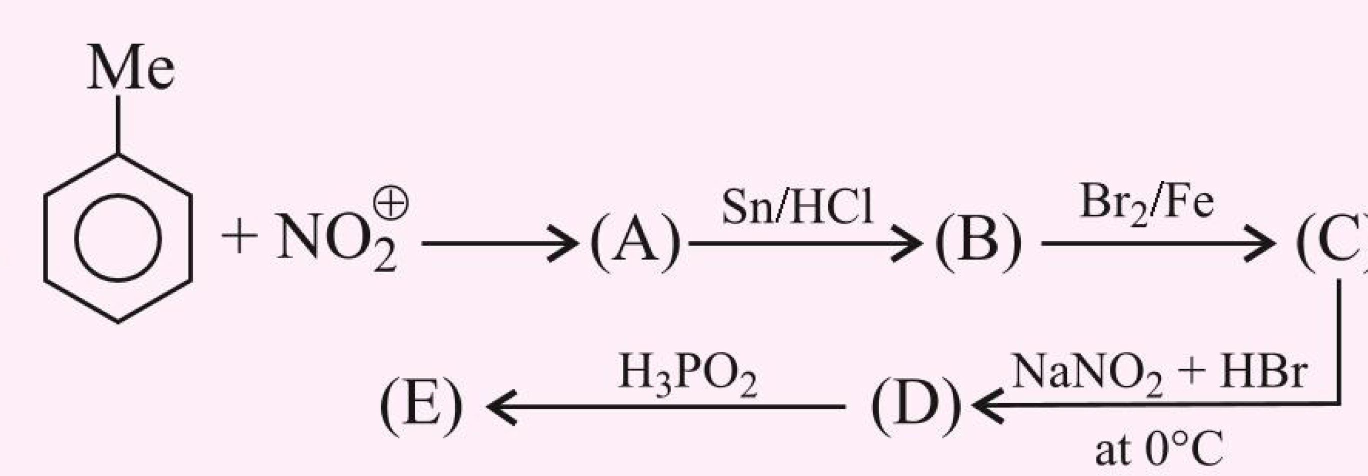
k. $(B) \xleftarrow[\overset{\ominus}{O}H,\ \text{at } 0°C]{\alpha\text{-Naphthol}} PhN_2Cl + \beta\text{-Naphthol} \xrightarrow[\text{at } 0°C]{\overset{\ominus}{O}H,} (A)$

l. 

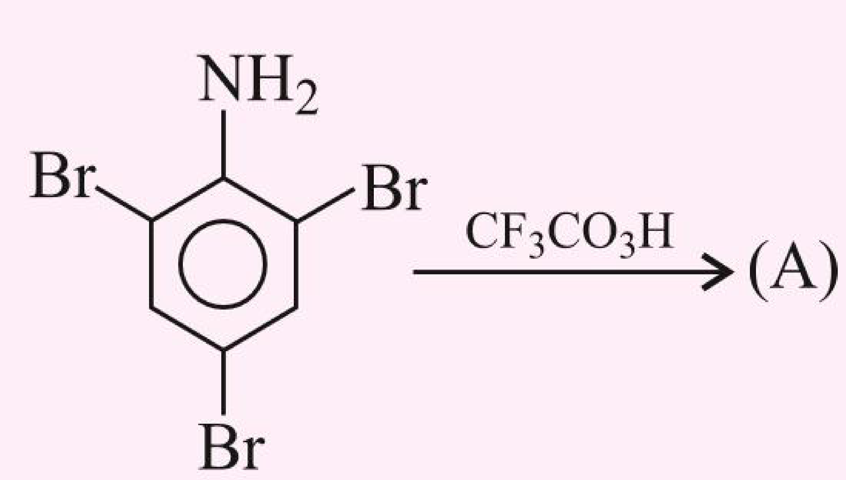
m. 

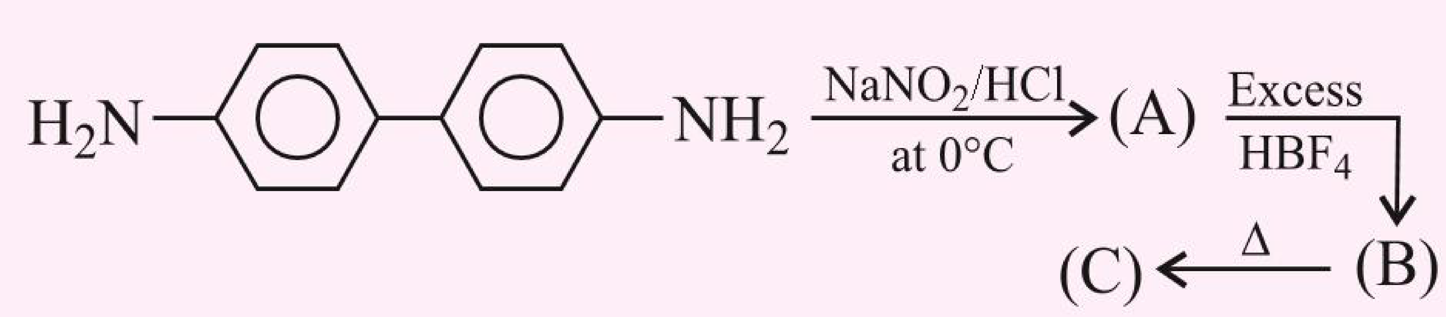
n. 

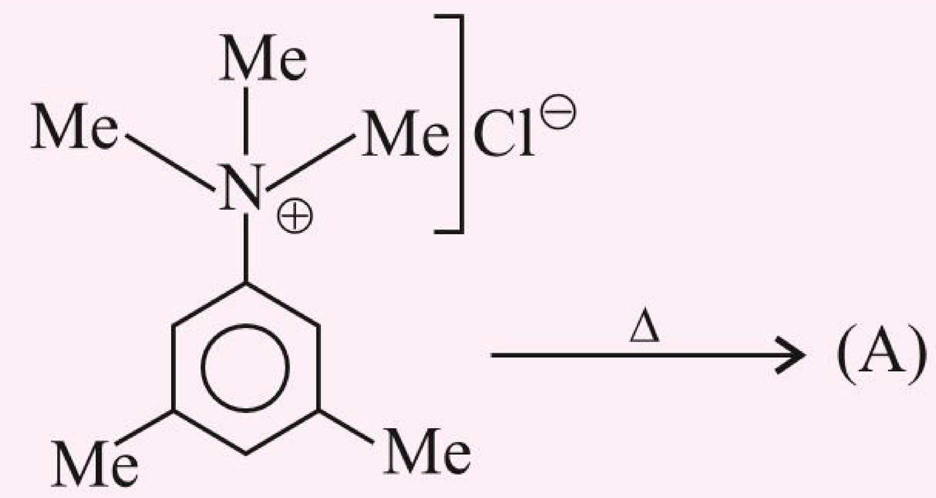
o. 

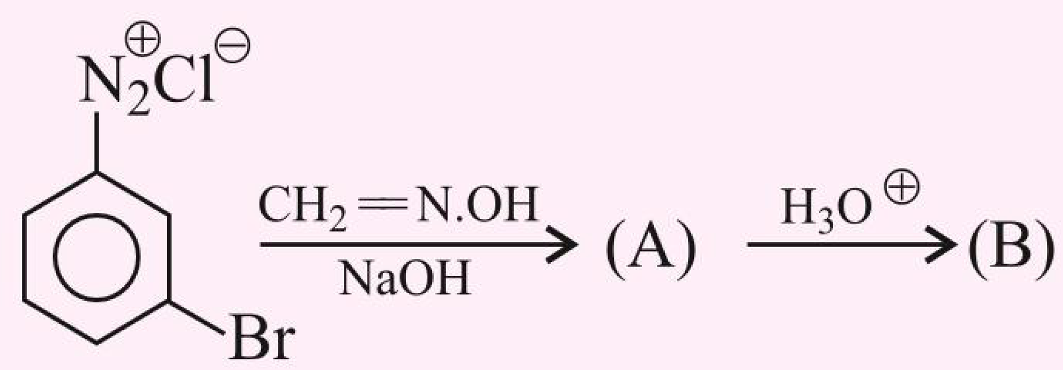
p. 

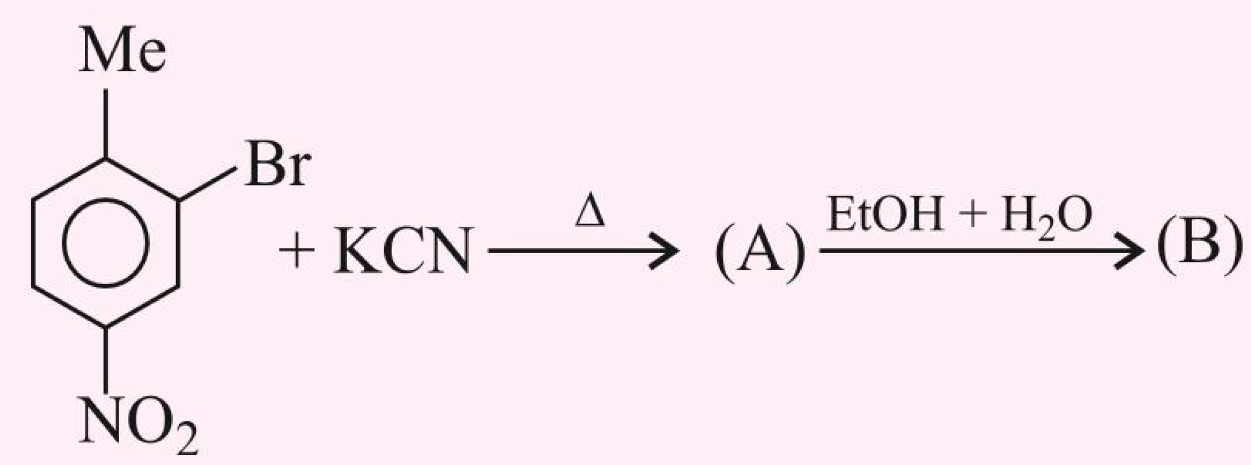
q. $PhN_2Cl + \underset{\text{Formaldoxime}}{CH_2{=}N.OH} \xrightarrow{H_3O^{\oplus}} (A)$

r. 

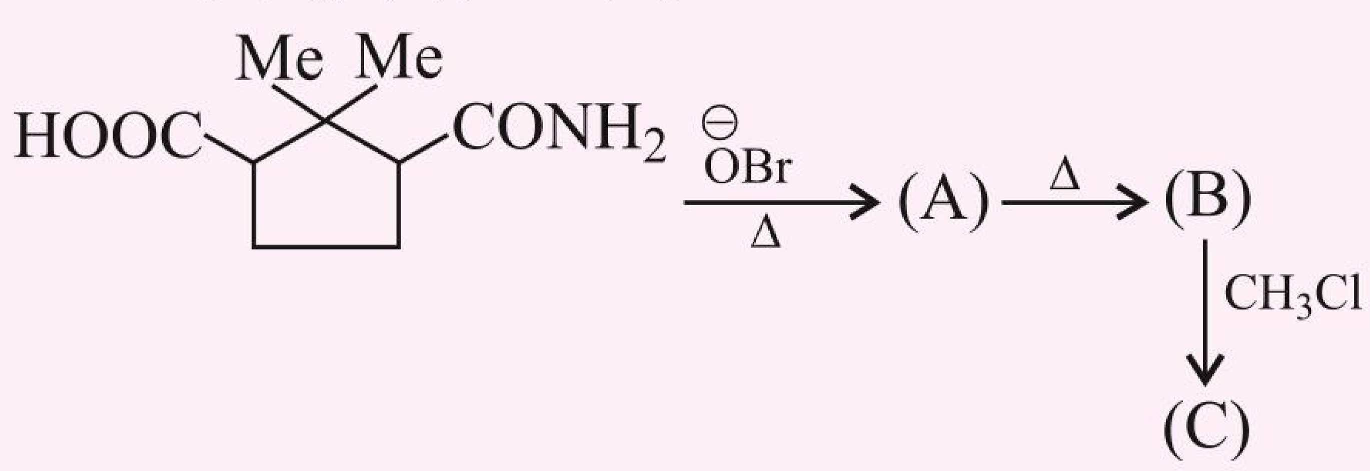
s. 

t. 

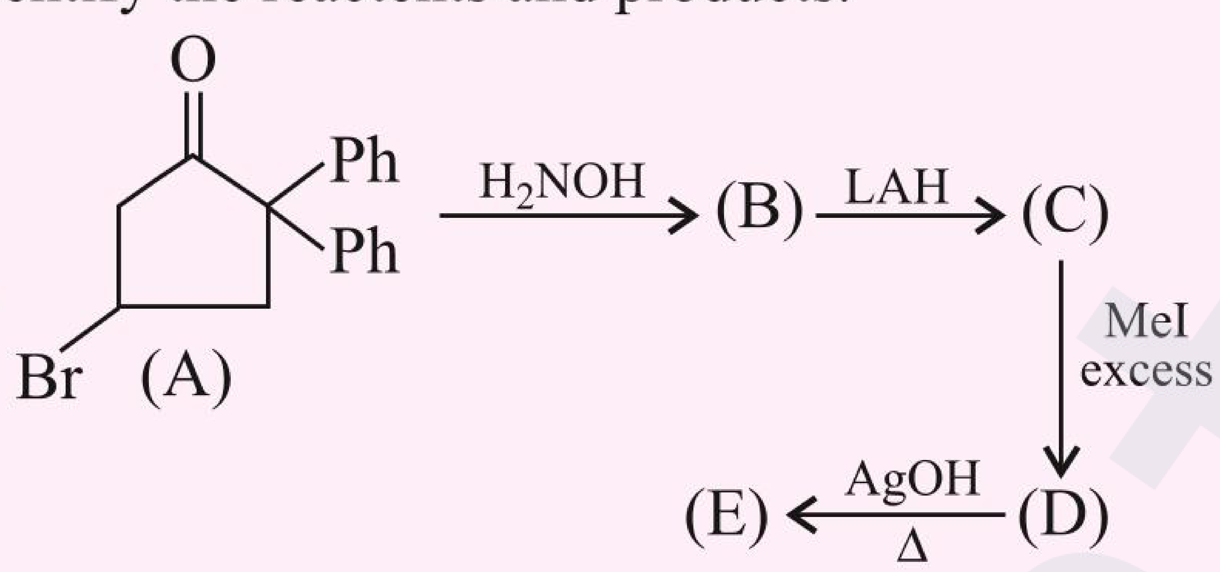
u. 

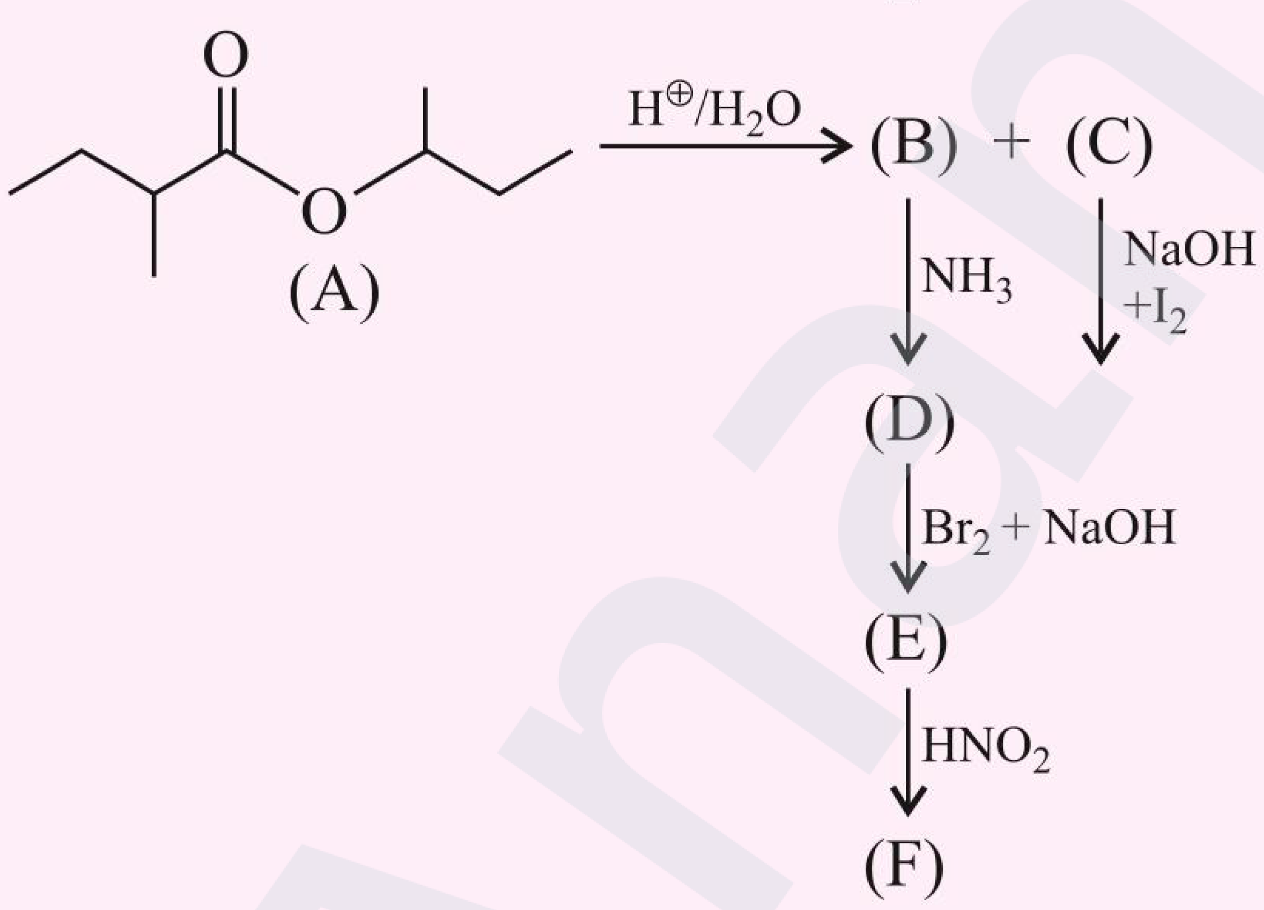
v. 

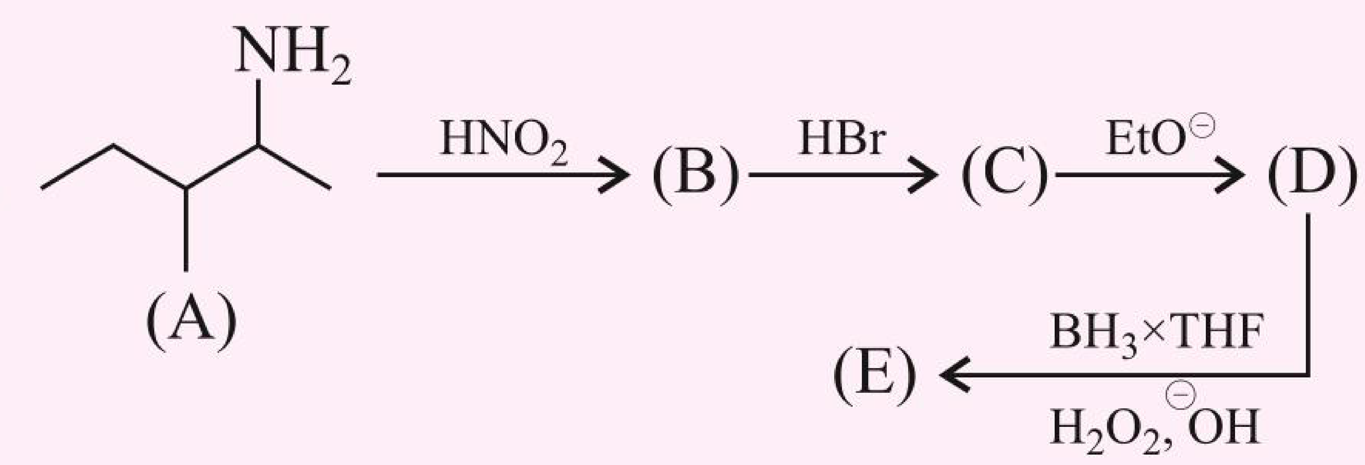
4. Identify (A), (B), and (C).

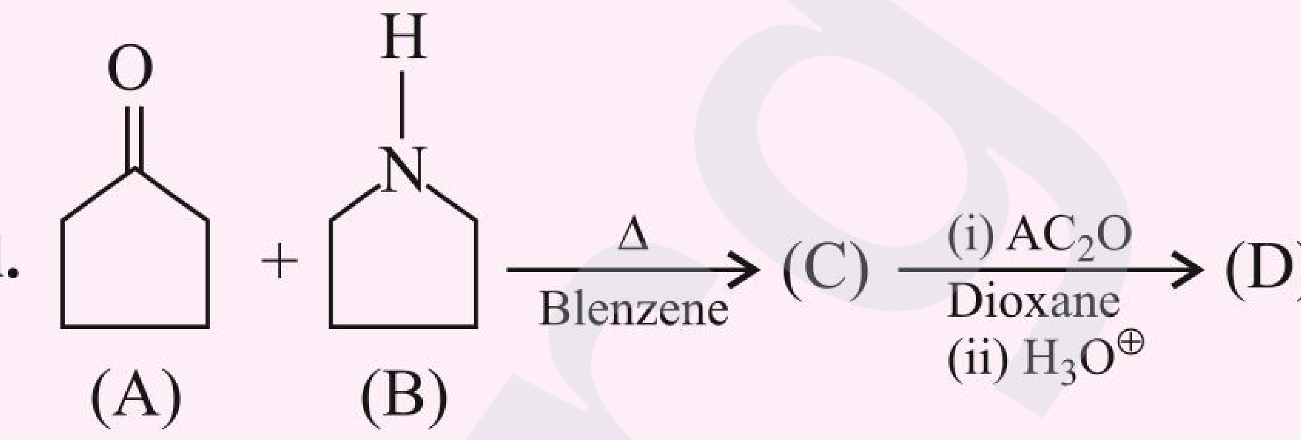


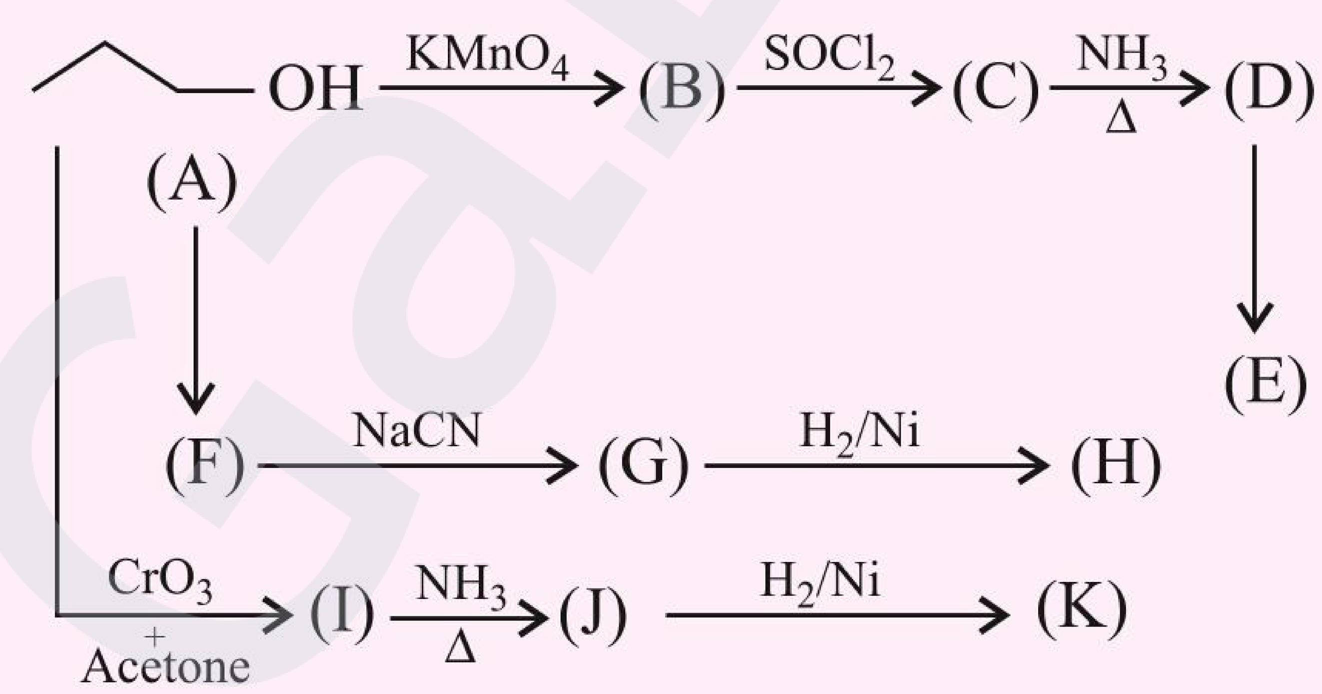
5. Identify the reactents and products.

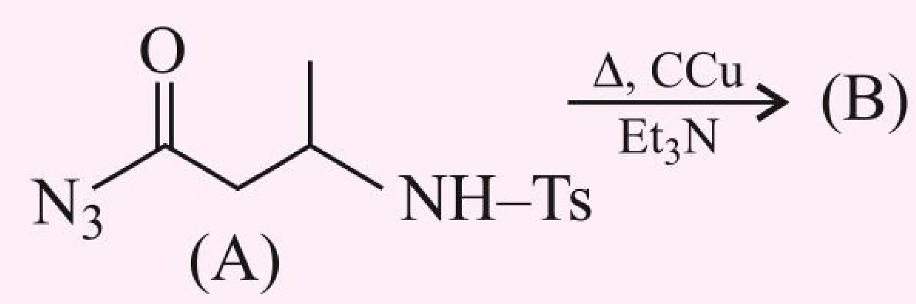
a. 

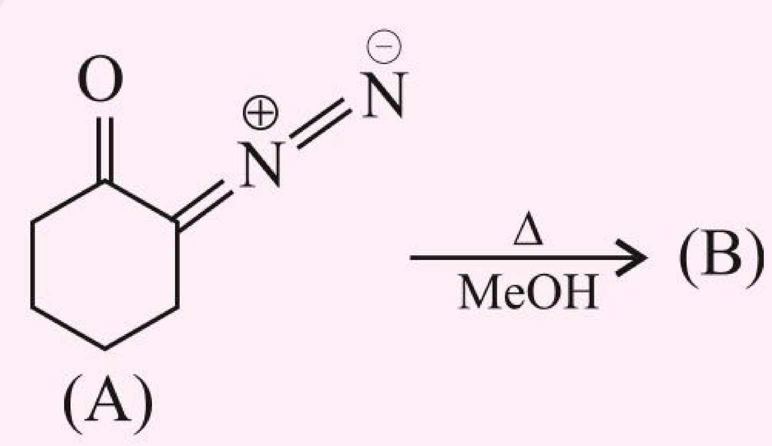
b. 

c. 

d. 

e. 

f. 

g. 

Exercises

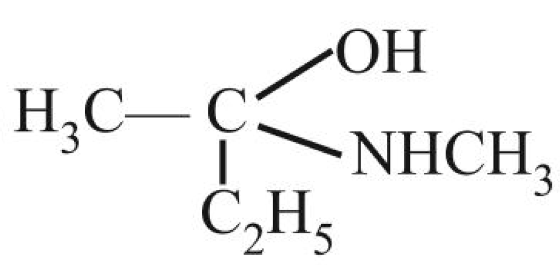
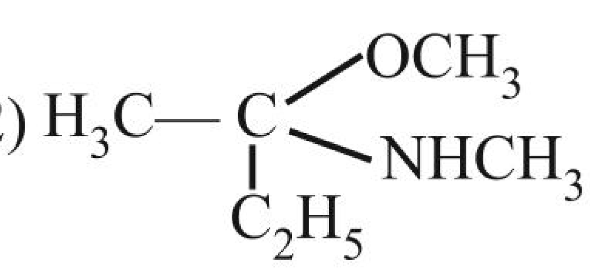
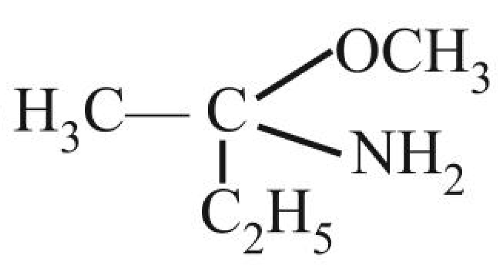
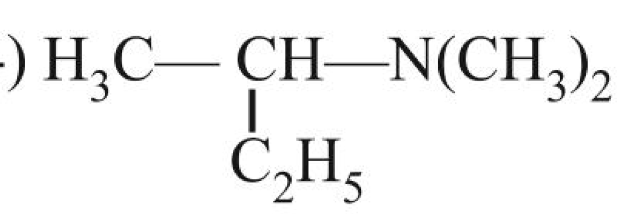
Single Correct Answer Type

Preparation and Properties of Amines

1. Consider the following reaction,

$$H_3CCOC_2H_5 + HCON(CH_3)_2 \xrightarrow{\Delta} X + CO_2$$

The product X is :

(1) 
(2) 
(3) 
(4) 

2. Acetone on reaction with ammonium formate at 180º–200ºC, gives:
(1) Propylamine (2) Ethylamine
(3) Propan-2-amine (4) Ethyl methylamine

3. When isobutene is reacted with HCN and H_2SO_4 followed by hydrolysis, it gives 1º amine and a side product (X). X is :
(1) 3º amine (2) Alkyl cyanide
(3) HCOOH (4) CH_3COOH

4. When 3º alcohol reacts with HCN and H_2SO_4 followed by hydrolysis, the product is :
(1) 3º amine (2) 2º amine
(3) 1º amine (4) Alkyl cyanide

5. 1º, 2º and 3º amines can be best distinguished by :
(1) HNO_2 treatment (2) Exhaustive alkylation
(3) Mustard oil reaction (4) Carbylamine reaction

6. Primary, secondary, tertiary amines can be separated by the following except :
(1) Fractional distillation
(2) Fractional method using diethyl oxalate
(3) Hinsberg's method using $C_6H_5SO_2Cl_2$
(4) Selective crystallisation

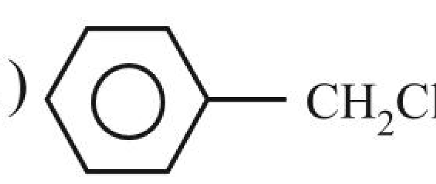
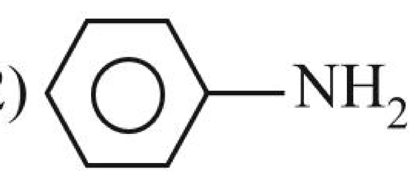
7. Which of the following reactions does not yield an amine ?
(1) $R—X + NH_3 \longrightarrow$
(2) $R—CH{=}NOH + [H] \xrightarrow[C_2H_5OH]{Na}$
(3) $R—CN + H_2O \xrightarrow{H^{\oplus}}$
(4) $R—CONH_2 + 4[H] \xrightarrow{LiAlH_4}$

8. Hinsberg's reagent is :
(1) C_6H_5COCl (2) CH_3COCl
(3) $C_6H_5CH_2Cl$ (4) $C_6H_5SO_2Cl$

9. Gabriel synthesis is used for the preparation of :
(1) 1º amine (2) 2º amine
(3) 3º amine (4) All of these

10. Which one of the following is best catalyst for the reaction shown below ?

$$CH_3(CH_2)_8CH_2Br \xrightarrow[\text{Benzene}]{KCN} CH_3(CH_2)_8CH_2CN$$

(1) 
(2) 
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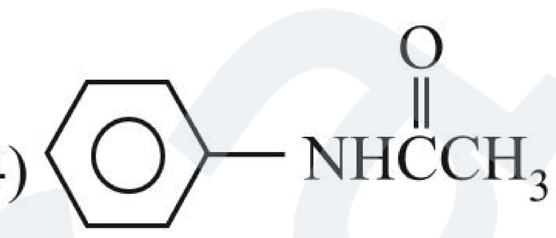
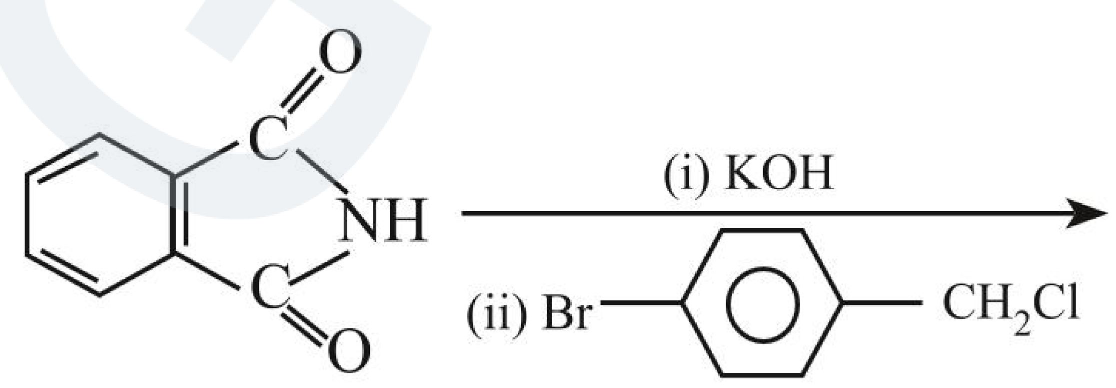
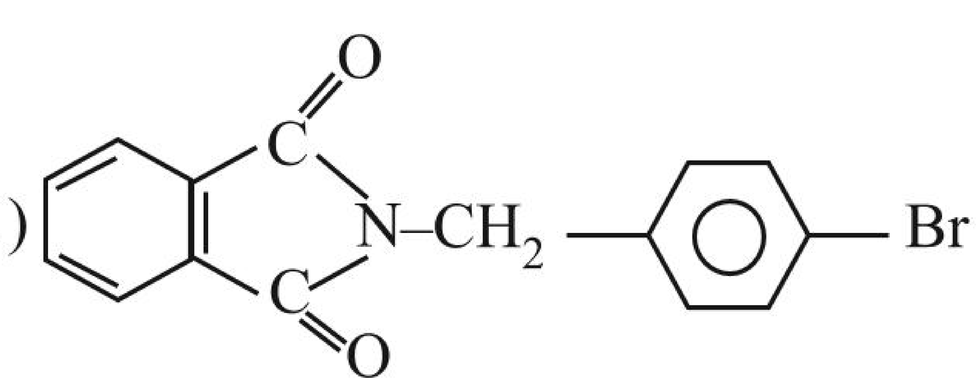
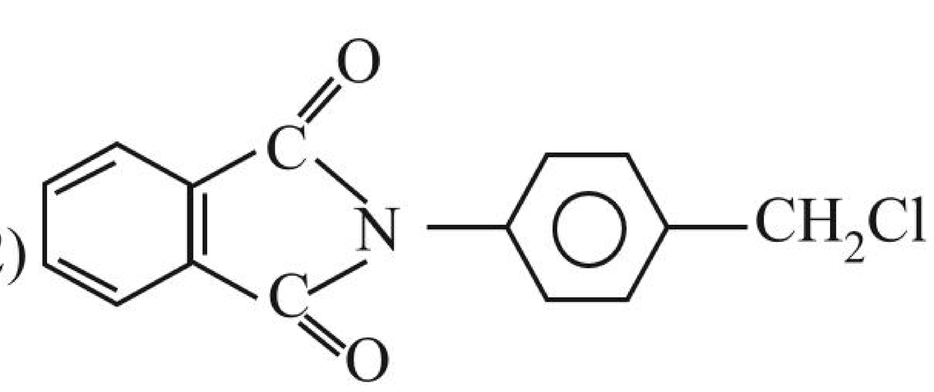
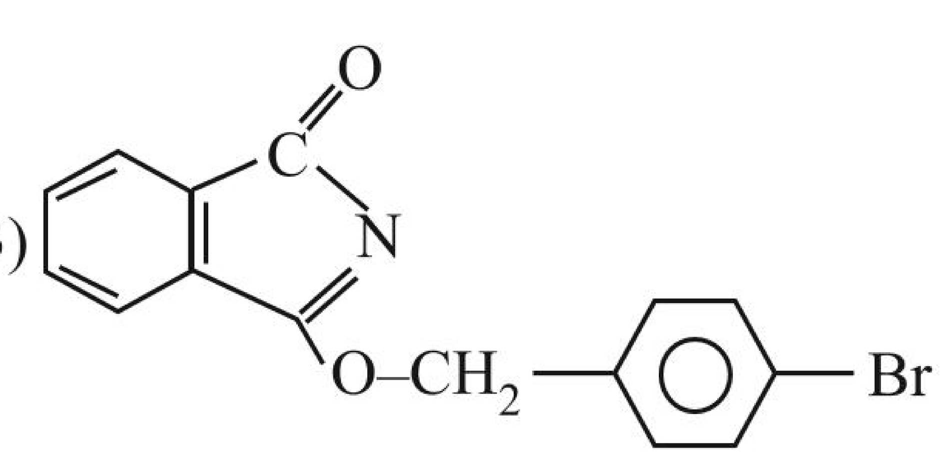
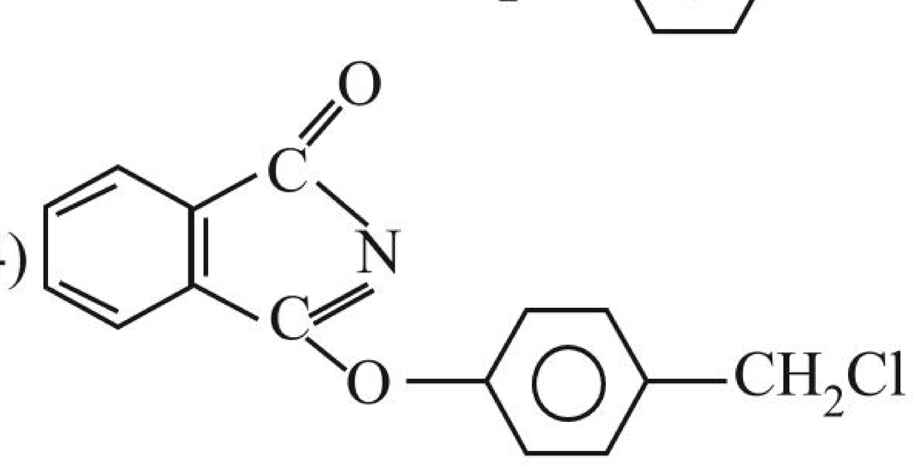
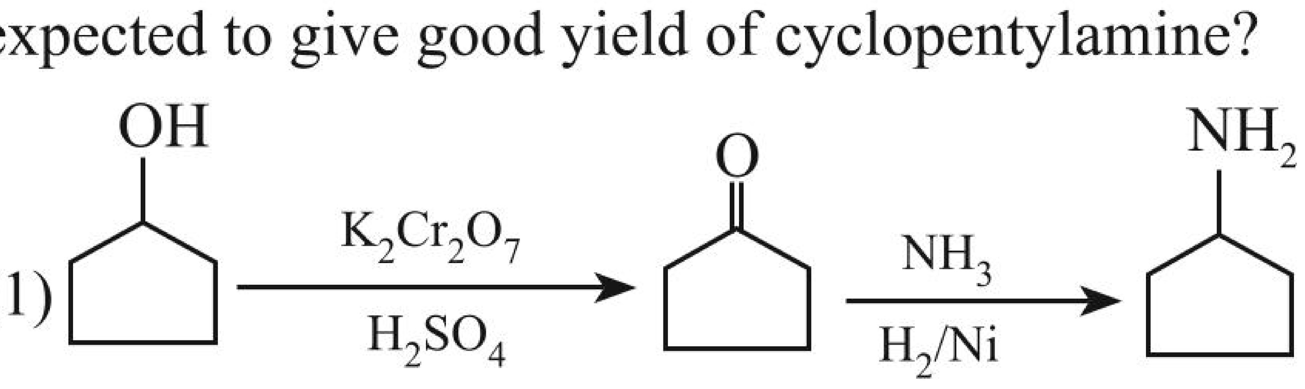
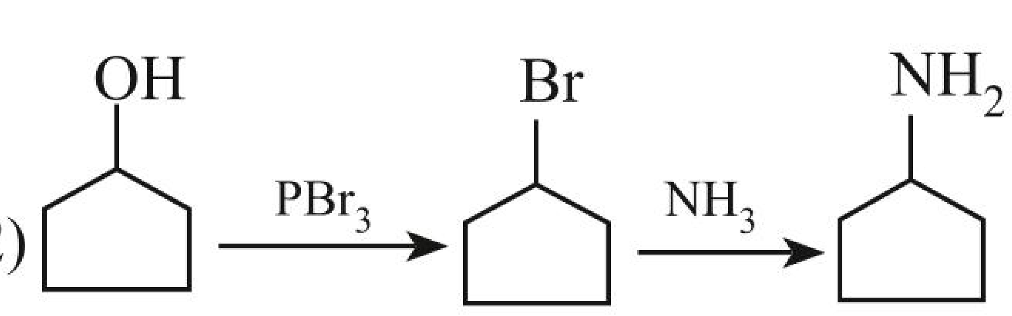
(4) 

11. The major product of the following reaction is :



(1) 
(2) 
(3) 
(4) 

12. Cyclopentanol can be converted into cyclopentylamine by following two routes. Which of the following methods is expected to give good yield of cyclopentylamine?

(1) 
(2) 

(3) Both are equally suitable

(4) Neither of the two.

13. Ethanamide is treated separately with the following reagents. Which one of these give methylamine?

(1) Hot concentrated H_2SO_4

(2) Sodalime

(3) $NaOH + Br_2$

(4) PCl_5

14. Which one of the following is used as phase transfer catalyst?

(1) CH_3NH_2 (2) $[(CH_3)_4N^{\oplus}]I^{\ominus}$

(3) $(CH_3)_3CNO_2$ (4) $(CH_3)_3N$

15. In the given reaction sequence,

$$C_6H_5CH_2NH_2 \xrightarrow[\Delta]{CH_3Cl/\text{Alc. KOH}} (A) \xrightarrow{H_2O/\overset{\ominus}{O}H} (B)$$

B is:

(1) $C_6H_5—CH_2OH$ (2) C_6H_5NC

(3) $C_6H_5—CH_2—NH_2$ (4) $C_6H_5—CN$

16. Which is the best method of preparing 2º amine ?

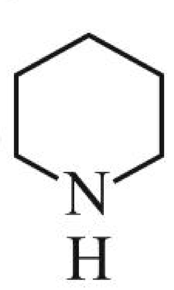
(1) $CH_3NH_2 \xrightarrow[\Delta]{CHCl_3/KOH} \xrightarrow{Sn/HCl}$

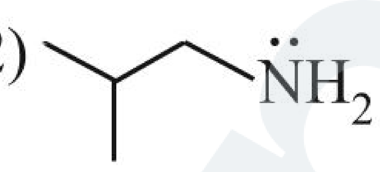
(2) $CH_3Cl \xrightarrow{KCN} \xrightarrow{Sn/HCl}$

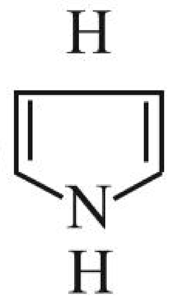
(3) $CH_3Cl \xrightarrow{KCN} \xrightarrow{LiAlH_4}$

(4) $CH_3Cl + NH_3 \longrightarrow$

17. Which of the following amines will react with cyclohexanone to give enamine ?

(1) 

(2) 

(3) 

(4) CH_3NH_2

18. Ethyl cyanide (A) can be converted to ethyl amine (B) by :

(1) $A \xrightarrow{Sn/HCl} B$

(2) $A \xrightarrow{H_3O^{\oplus}} \xrightarrow{NH_3/\Delta} \xrightarrow{KBrO/\Delta} B$

(3) $A \xrightarrow{LiAlH_4} B$

(4) both (1), (3) are correct

19. In Gabriel synthesis, halide may be:

(1) Benzyl halide (2) Allyl halide

(3) Both (1) and (2) (4) Tertiary alkyl halide

20. In Gabriel synthesis, amine is always:

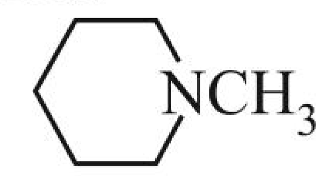
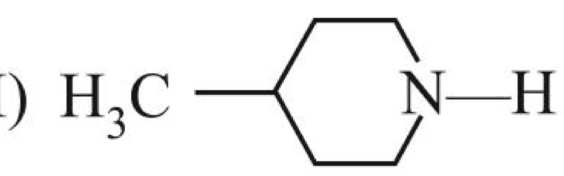
(1) Aliphatic primary amine

(2) Aliphatic secondary amine

(3) Aromatic primary amine

(4) Aromatic secondary amine

21. Predict about the relative boiling point of the following two amines.

(I)  (II) 

(1) Boiling point of I > II

(2) Boiling point of II > I

(3) Both should have equal boiling points.

(4) It can't be predicted.

22. Which of the following statements is not correct?

(1) Primary amine show intermolecular hydrogen bonding.

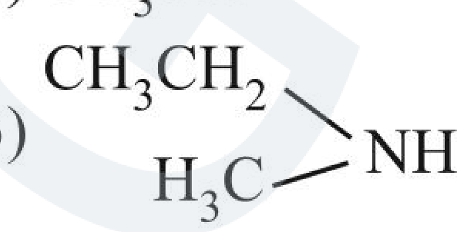
(2) Secondary amines show intermolecular hydrogen bonding.

(3) Tertiary amines show intermolecular hydrogen bonding.

(4) Amines have lower boiling points as compared to those of alcohols and carboxylic acids of comparable molar masses.

23. Which is most volatile?

(1) CH_3OH (2) $(CH_3)_3N$

(3)  (4) $CH_3CH_2CH_2NH_2$

24. Which is the best leaving group?

(1) $CH_3COO^{\ominus}$ (2) $\overset{\ominus}{N}H_2$

(3) $\overset{\ominus}{O}H$ (4) $—\overset{\oplus}{N}\equiv N$

25. Which of the following statements is not correct?

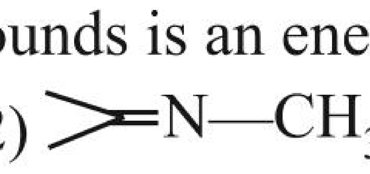
(1) The aryl group in aryl ammonium ion less stabilizes the ion relative to the amine.

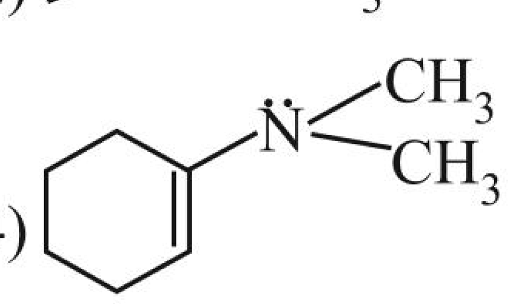
(2) The alkyl group in alkyl ammonium ion more stabilizes the ion relative to the amine.

(3) Aromatic amines are stronger bases than ammonia.

(4) Aliphatic amines are stronger bases than ammonia.

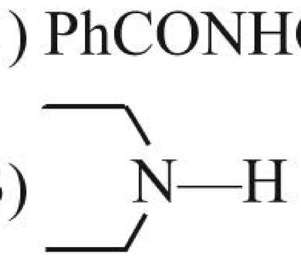
26. Which of the following compounds is an enemine?

(1) PhN=NH (2) 

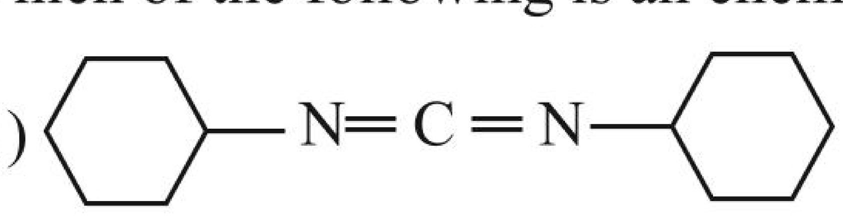
(3) PhN=NPh (4) 

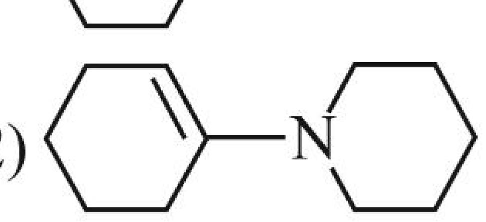
27. Which of the following compounds is an imine?

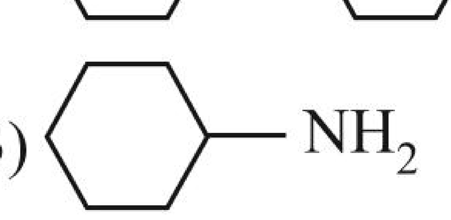
(1) PhCONHCOPh (2) $C_2H_5N=CH_2$

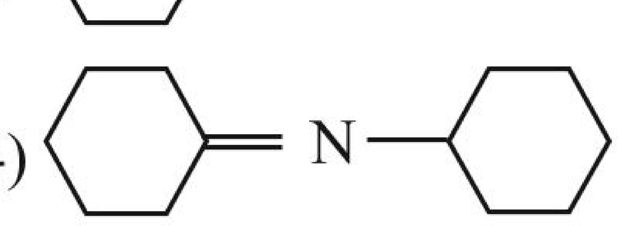
(3)  (4) $PhCONH_2$

28. Which of the following is an enemine?

(1) 

(2) 

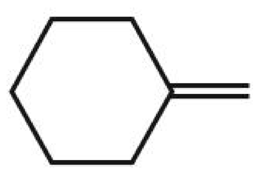
(3) 

(4) 

29. Predict the nature of A in the following reaction:

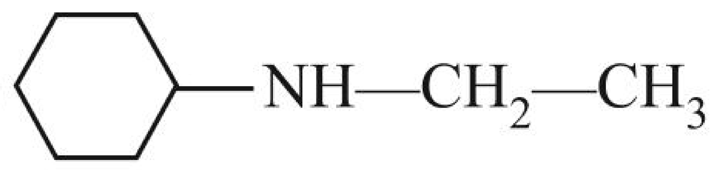
$(CH_3)_3CCH_2NH_2 \xrightarrow{HONO}$ A (main product)

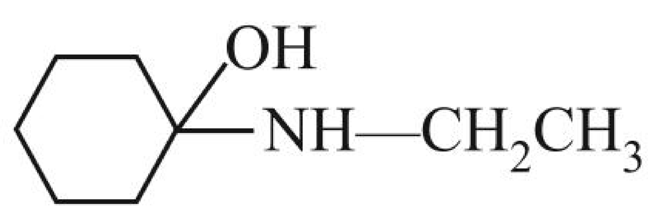
(1) $(CH_3)_3CCH_2OH$ (2) $(CH_3)_3CCH = CH_2$
(3) $(CH_3)_3C(OH)C_2H_5$ (4) $(CH_3)_3CCH_2NH(NO)$

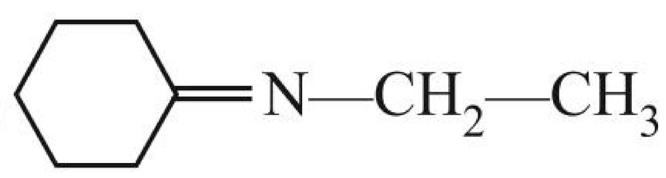
30.  $=O + CH_3CHNH_2 \xrightarrow{pH = 5.0} A \xrightarrow{H_2,\ Ni} B$

Final product B is:

(1) 

(2) 

(3) 

(4) 

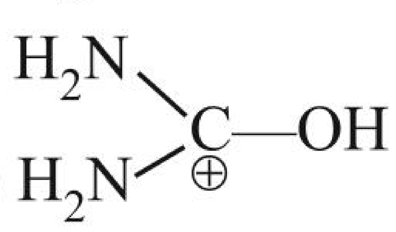
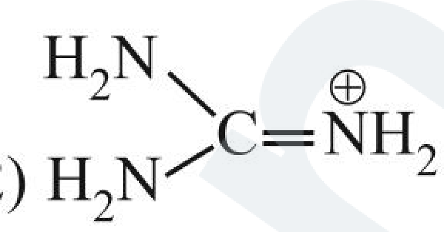
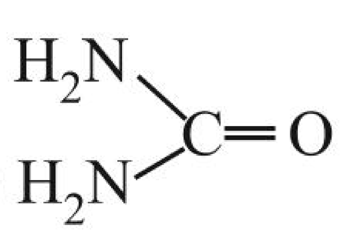
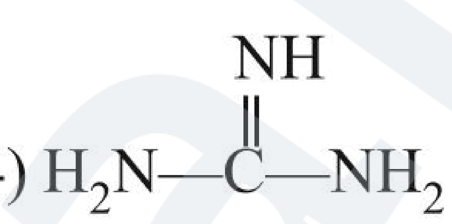
31. Decreasing order of basicity of the three isomers of nitro anline is:

(1) *m* - nitroaniline > *o*- nitroaniline > *p* - nitroaniline
(2) *m*- nitroaniline > *p* - nitroaniline > *o* - nitroaniline
(3) *p*- nitroaniline > *m* - nitroaniline > *o*- nitroaniline
(4) *p*-nitroaniline > *o*- nitroaniline > *m*- nitroaniline

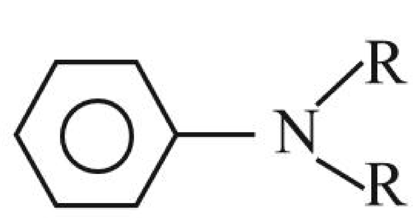
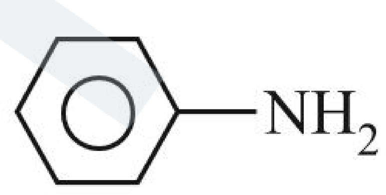
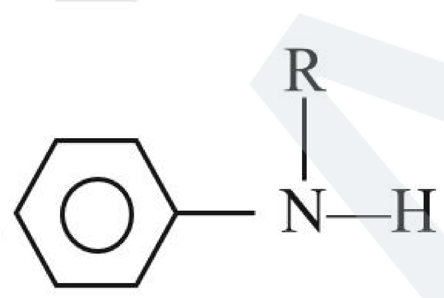
32. The correct sequence regarding base strength of aliphatic amines in aqueous solution is:

(1) $RNH_2 > R_2NH > R_3N > NH_3$
(2) $R_2NH > RNH_2 > R_3N > NH_3$
(3) $R_2NH > R_3N > RNH_2 > NH_3$
(4) $R_3N > R_2NH > RNH_2 > NH_3$

33. Strongest base is:

(1)  (2) 
(3)  (4) 

34. Which of the following amines form N—nitroso derivative when treated with $NaNO_2$ and HCl?

(1)  (2) 
(3)  (4) CH_3NH_2

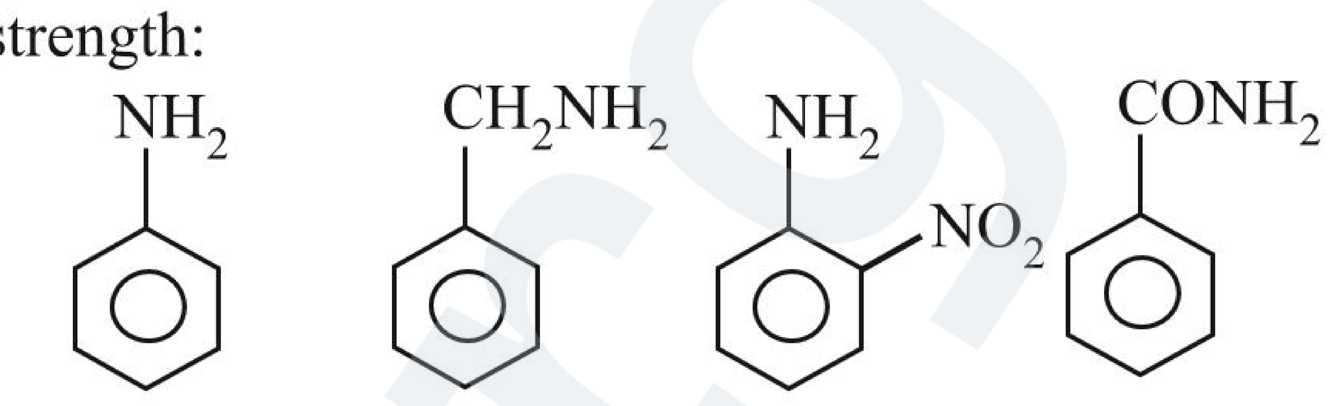
35. Pick up the correct statement:

(1) The boiling of alkyl halides are more than those of the corresponding alkanes.
(2) In water, the solubility of $CH_3OH > C_2H_5OH > C_6H_5OH$.
(3) $C_6H_5NH_2$ is a weaker base than NH_3.
(4) All the above statements are correct.

36. Which of the following are not functional isomers of each other?

(1) $CH_3CH_2NO_2$and $CH_3CH_2ON =O$
(2) C_2H_5CHO and CH_3COCH_3
(3) $CH_3CH_2NH_2$ and CH_3NHCH_3
(4) $C_3H_7NH_2$ and $(CH_3)_2CHNH_2$

37. Rank the following compounds in order of increasing basic strength:



1 2 3 4

(1) 4 < 2 < 1 < 3 (2) 4 < 3 < 1 < 2
(3) 4 < 1 < 3 < 2 (4) 2 < 1 < 3 < 4

38. Which of the following isomers of C_8H_9NO is the weakest base?

(1) *m*-Aminoacetopheone (2) *p*-aminoacetophenone
(3) *o*-Aminoacetophenone (4) Acetanilide

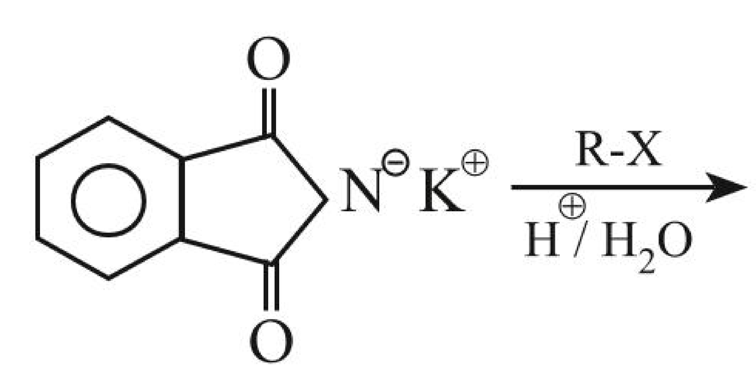
39. Of the following reactions, how many reactions, are used for the preparation of amines?

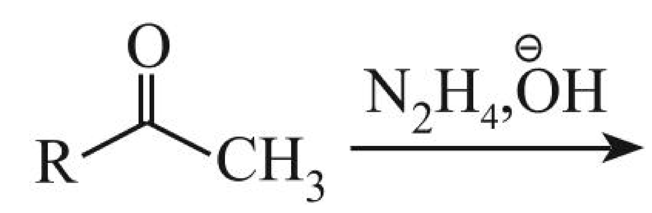
1. $R-C\equiv N \xrightarrow{LiAlH_4}$

2. $R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{LiAlH_4}$

3. $R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{Br_2 + \overset{\ominus}{O}H}$

4. $R-\overset{O}{\overset{\|}{C}}-CH_3 + H_3C-NO_2 \xrightarrow{NaOH}$

5. 

6. 

7. $R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[D]{P_2O_5}$

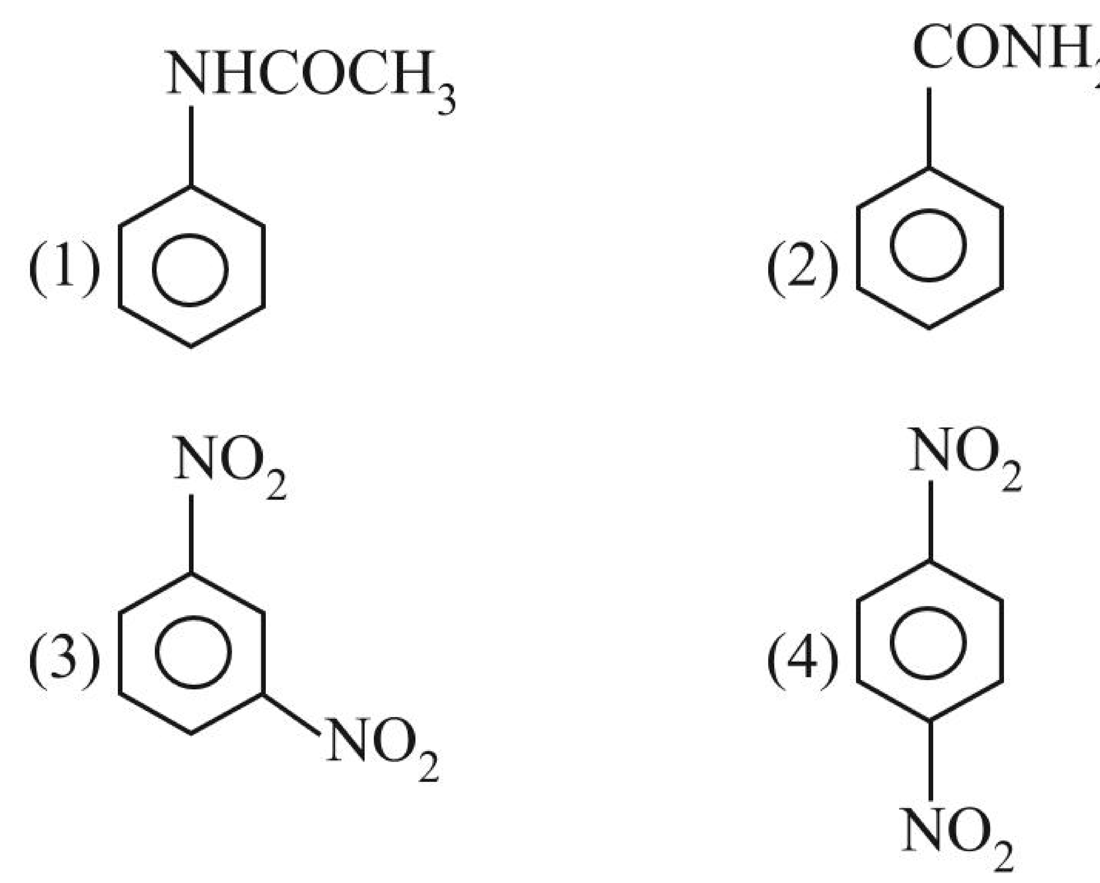
8. $R-CH_2-NO_2 \xrightarrow{H_2,Ni}$

(1) 7 (2) 6
(3) 5 (4) 4

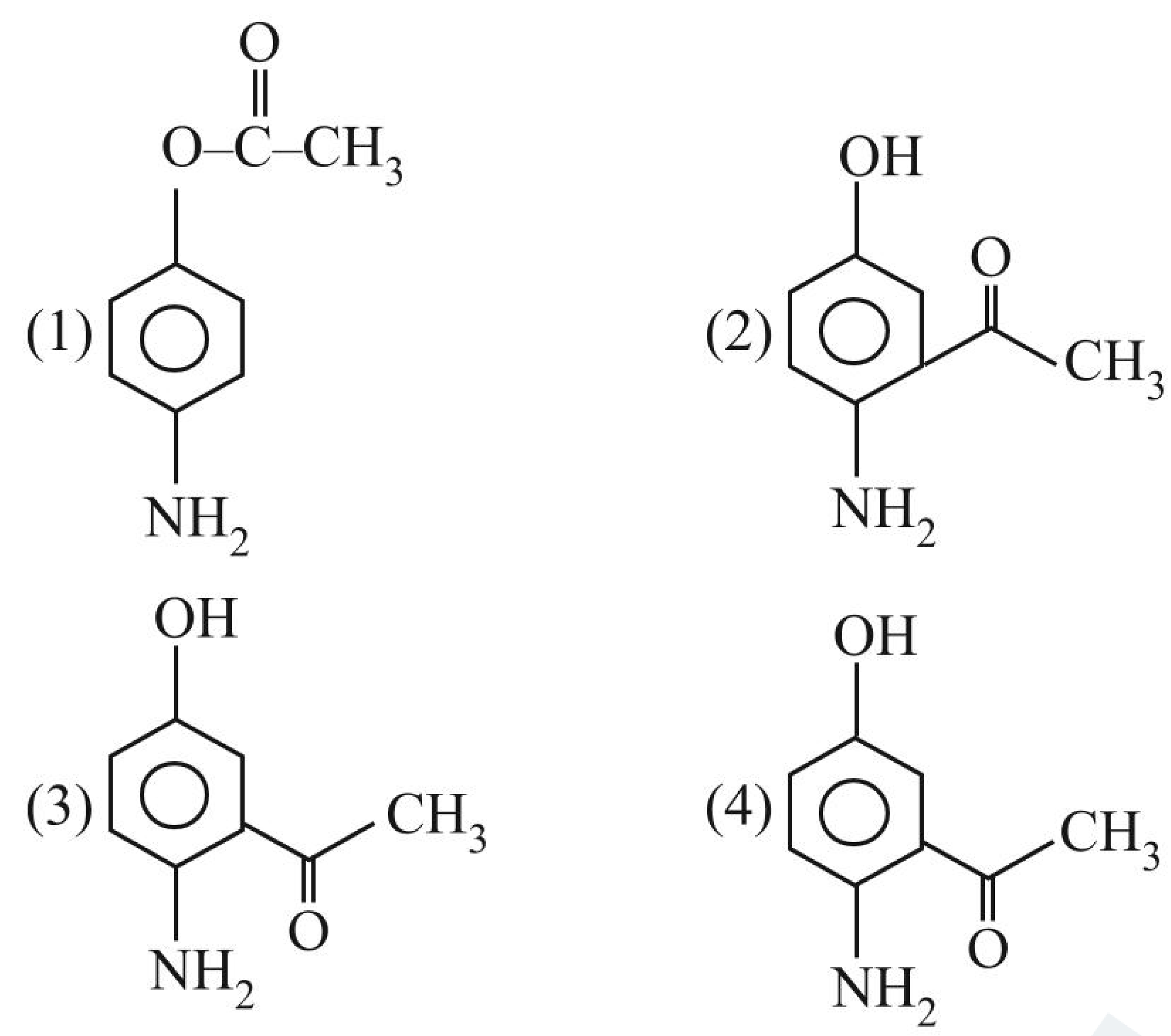
40. Which sequence of steps will be able to produce 3,3' dinitro-biphenyl from benzene?

(1) HNO_3/H_2SO_4, Cl_2/ $FeCl_3$, Na/ether
(2) Cl_2/ $FeCl_3$, HNO_3 / H_2SO_4, Na/ether
(3) $Cl_2/FeCl_3$, H_2SO_4, Na/ether
(4) I_2/HIO_3, Cl_2/ $FeCl_3$,$C_6H_5NO_2$

41. A neutral benzenoid nitrogenous organic compound has zero dipole moment, its probable structure is:



42. The reaction of *p*-aminophenol with one mole of acetyl chloride in presence of pyridine gives :



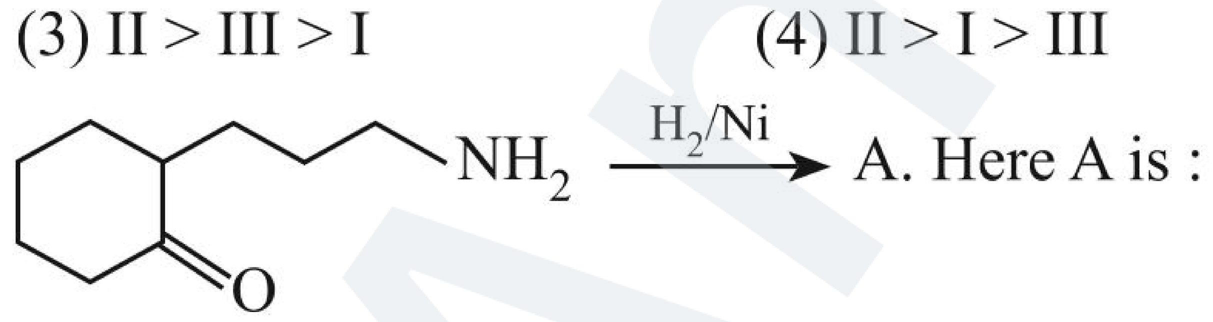
43. Which of the following is not a property of sulphanilic acid?

(1) It is soluble in aq. NaOH.
(2) It is soluble in aq. HCl.
(3) It is insoluble in organic solvents.
(4) It does not melt but decomposes.

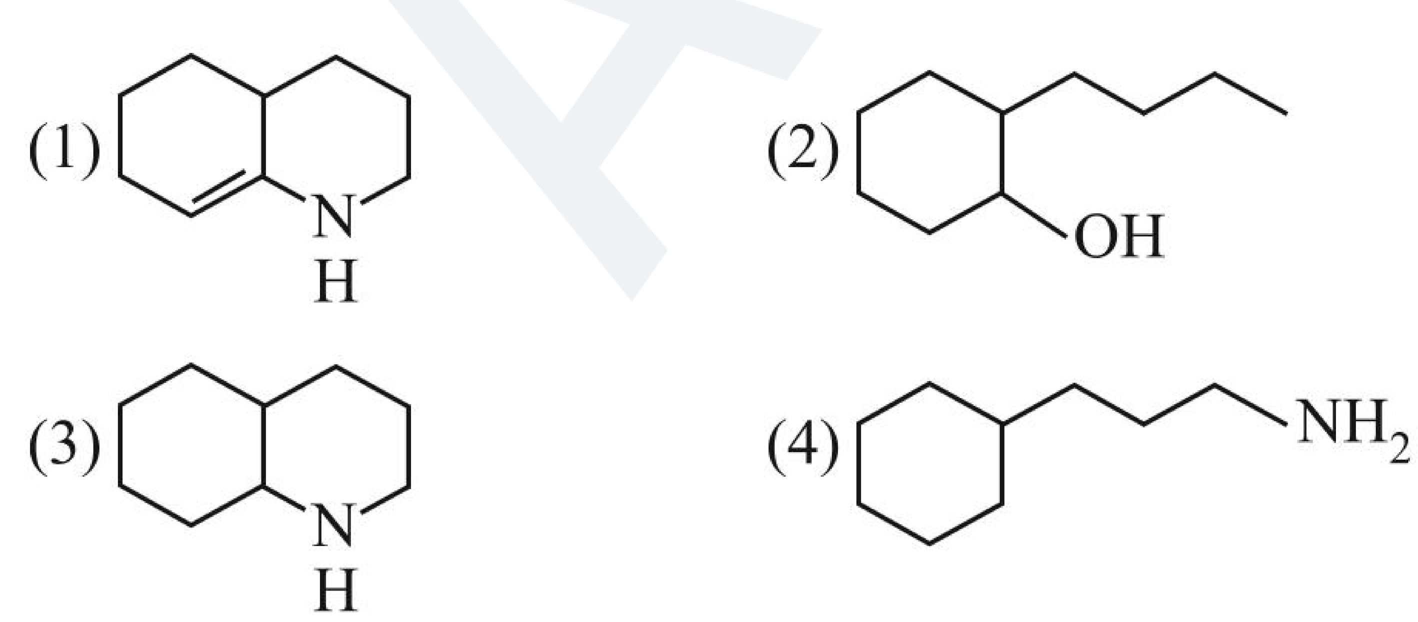
44. The correct arrangement of decreasing dipole moment of the following three compounds is:

CH_3CH_2OH (I); $CH_3CH_2NH_2$ (II); $CH_3CH_2CH_3$ (III)

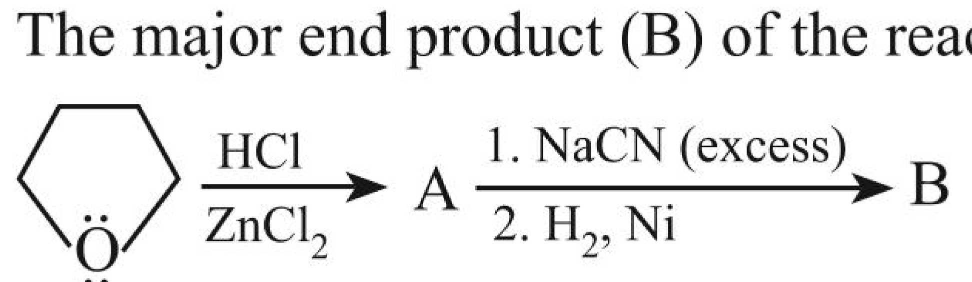
(1) I > II > III
(2) III > II > I
(3) II > III > I
(4) II > I > III

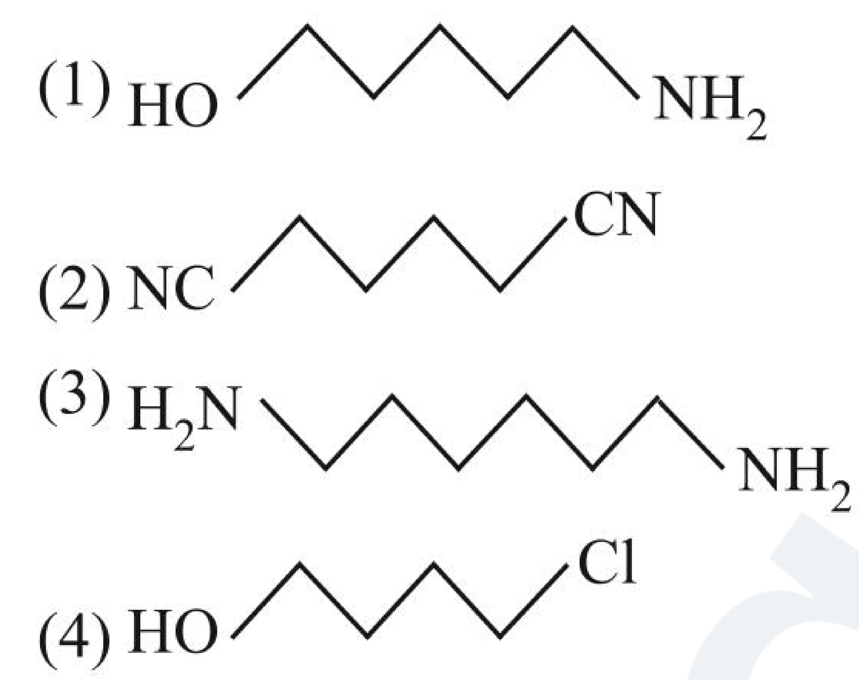
45. 

A. Here A is :



46. The major end product (B) of the reaction:



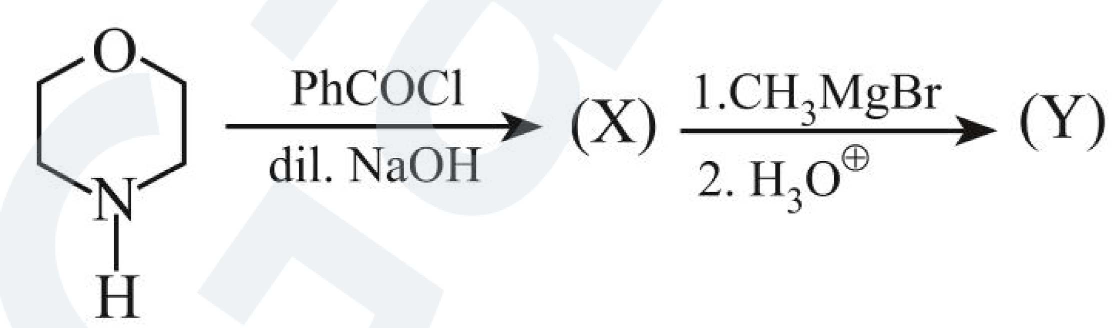


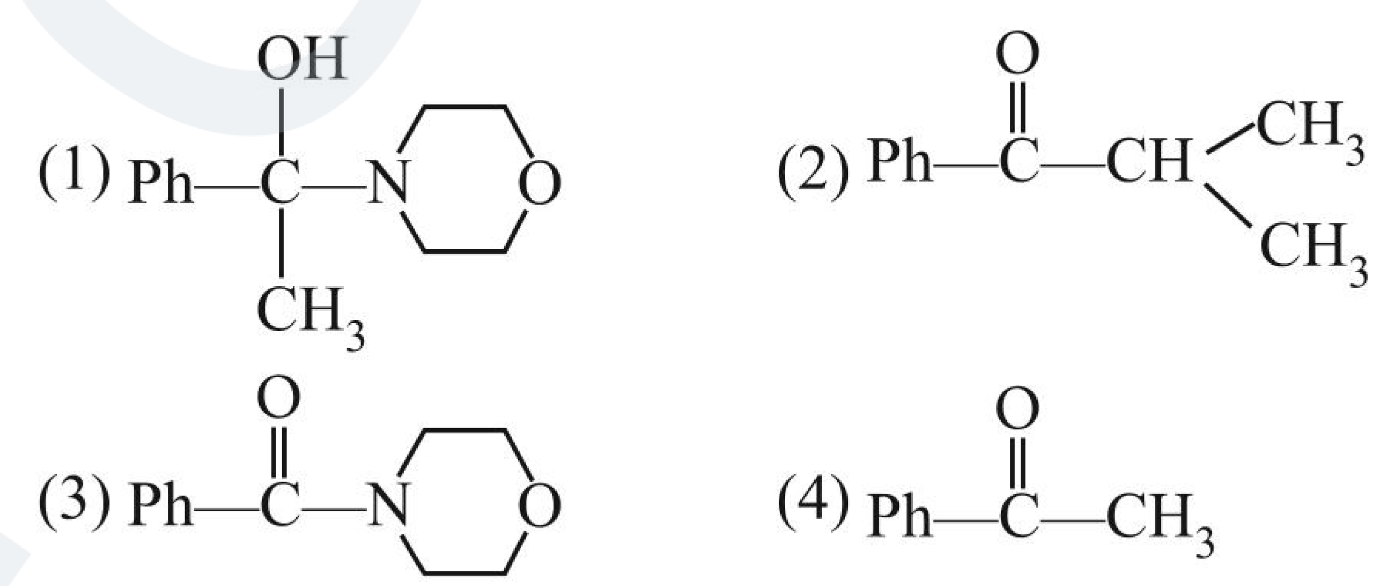
47. The end product (Y) of the reaction sequence:

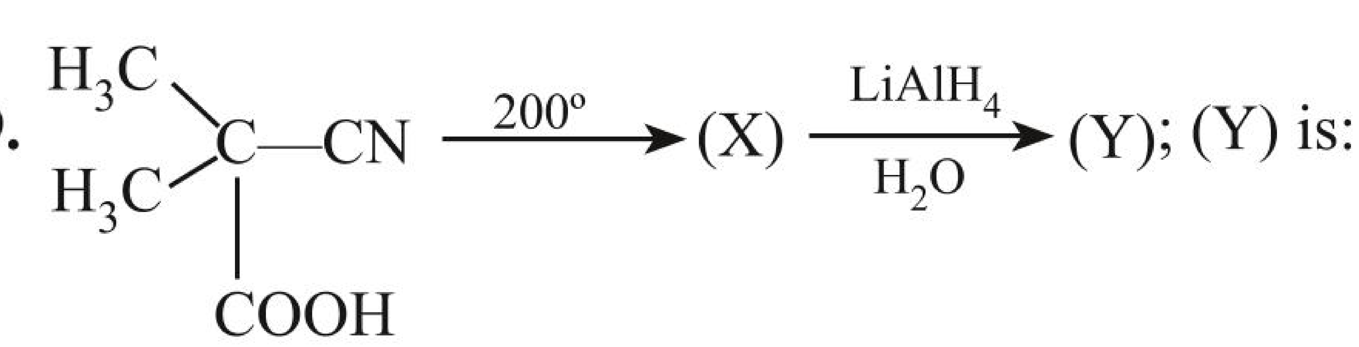
$$CH_3NHCH_3 \xrightarrow[NaOH]{PhCOCl} (X) \xrightarrow[H_2O]{LiAlH_4} (Y)$$

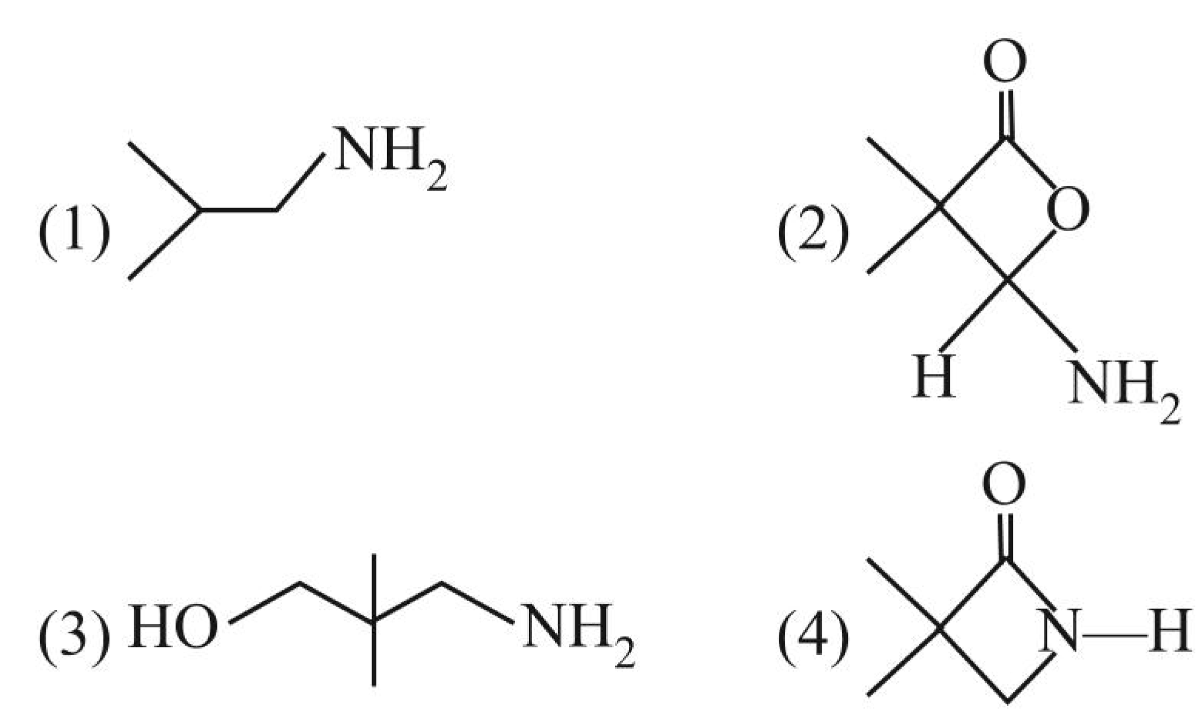
(1) $PhN(CH_3)_2$
(2) $PhCH_2N(CH_3)_2$
(3) $PhCH(OH)N(CH_3)_2$
(4) $PhCON(CH_3)_2$

48. The major product (Y) formed in the reaction sequence is:

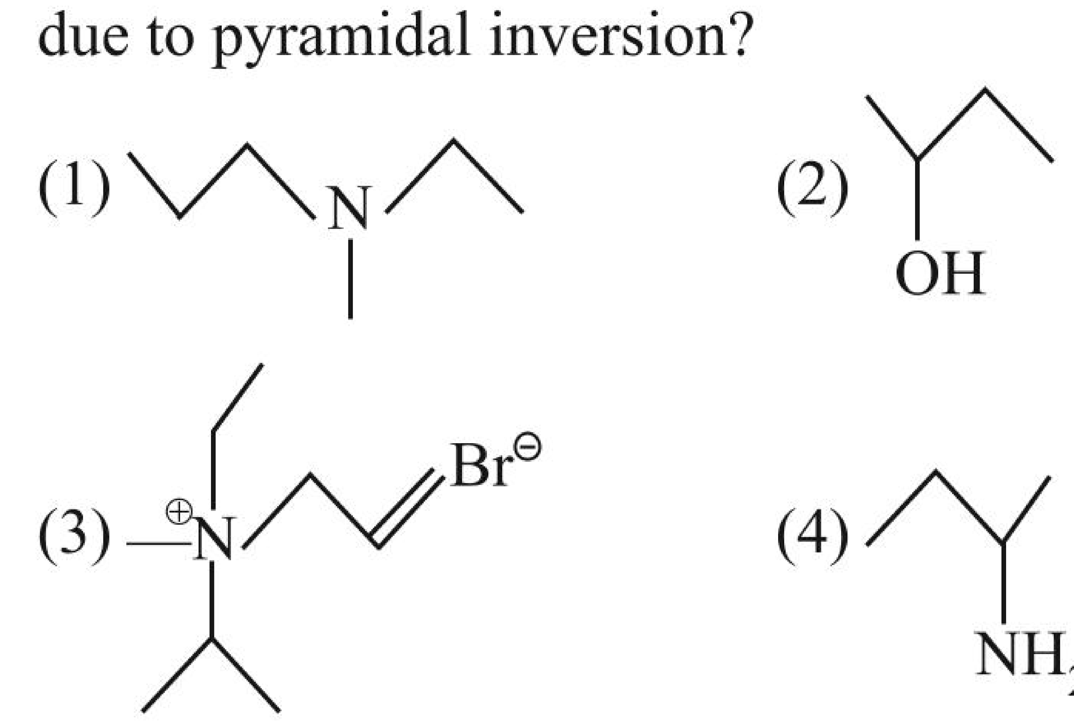




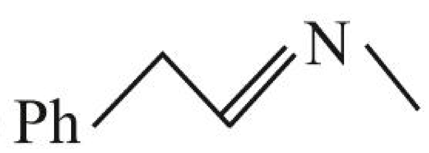
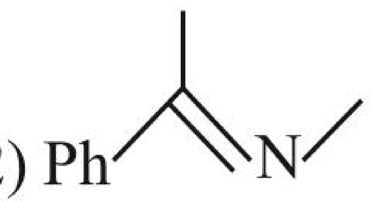
49. 

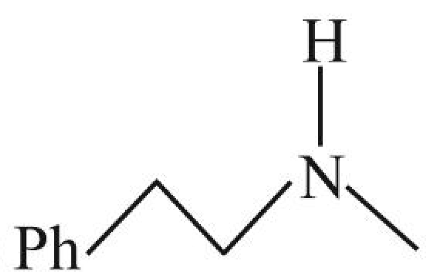
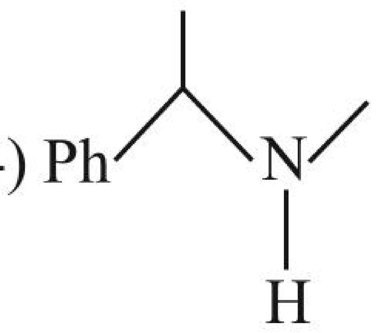


50. Which of the following compounds loses optical activity due to pyramidal inversion?

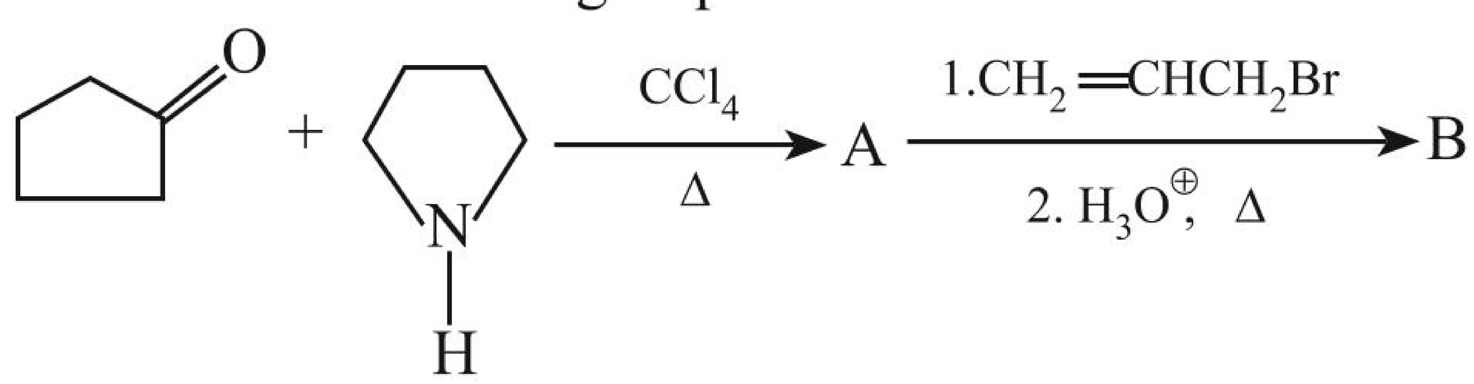


51. $Ph–C \equiv CH \xrightarrow[H_2O_2,\ \overset{\ominus}{O}H]{B_2H_6} A \xrightarrow[H_2,\ Ni,\ \Delta]{CH_3NH_2}$ B. The final product B is:

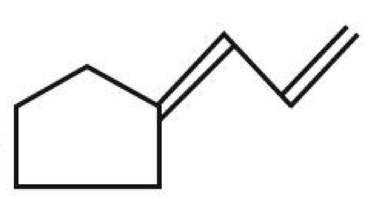
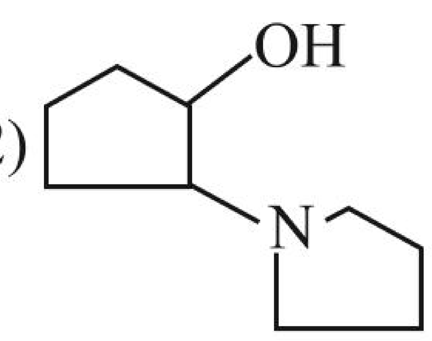
(1)  (2) 

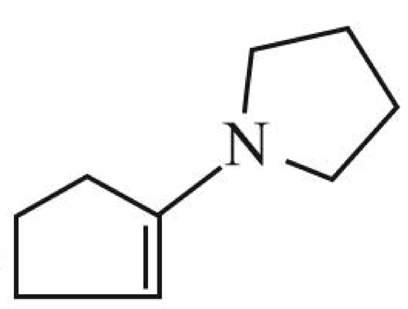
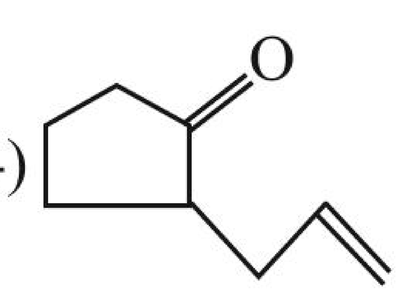
(3)  (4) 

52. Consider the following sequence of reactions:



The end product (B) is:

(1)  (2) 

(3)  (4) 

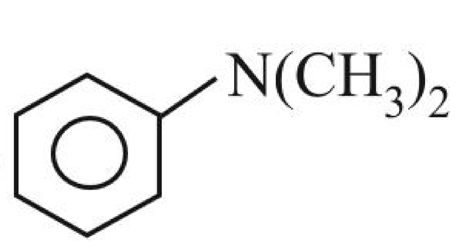
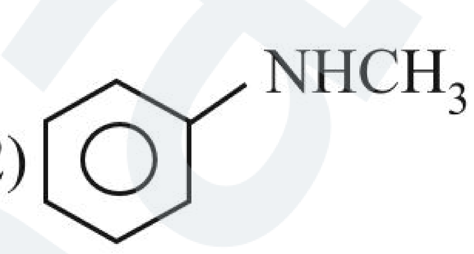
53. In which of the following reaction does the amine behaves as an acid?

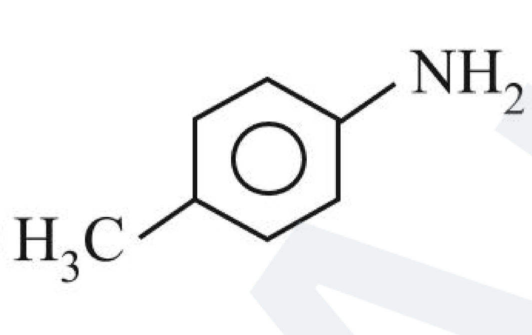
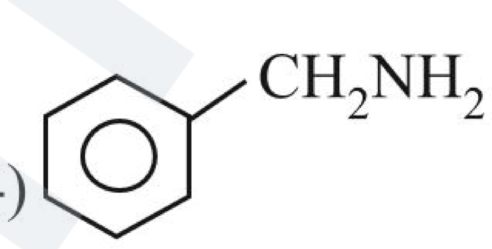
(1) $(C_2H_5)_3\ddot{N} + BF_3$ (2) $CH_3NH_2 + H_2O$

(3) $\left(\begin{matrix}H_3C\\H_3C\end{matrix}\!\!>CH\right)_2NH$ (4) $(C_2H_5)_2NH + H_2PtCl_6$

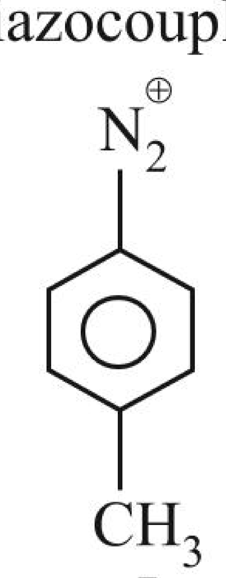
Diazotisation

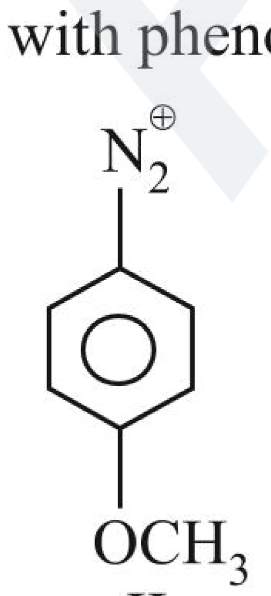
54. Amongst the compounds given, the one that would form a brilliant colored dye on treatment with $NaNO_2$ in dil. HCl followed by addition to an alkaline solution of β-naphthol is:

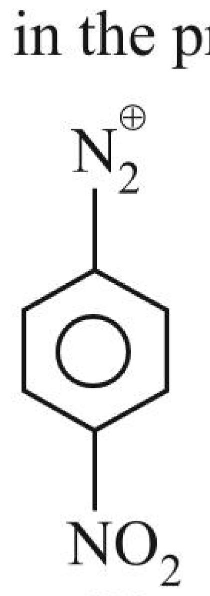
(1)  (2) 

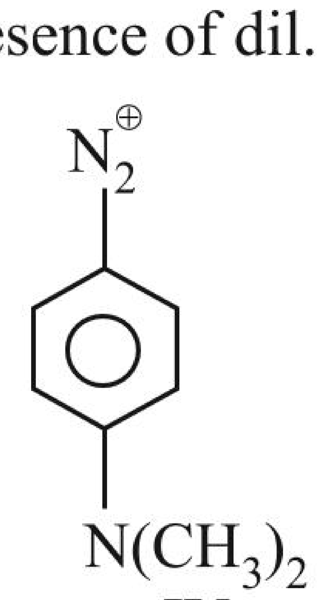
(3)  (4) 

55. For diazonium ions, the order of reactivity towards diazocoupling with phenol in the presence of dil. NaOH is:


I

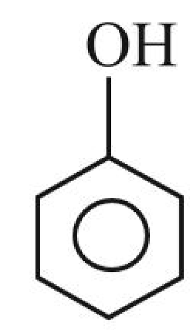

II

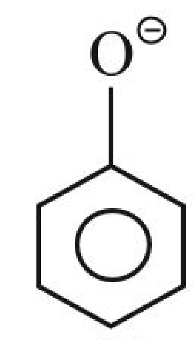

III

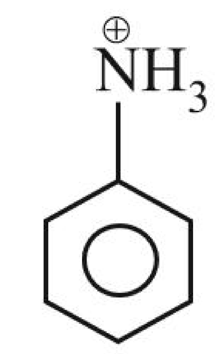

IV

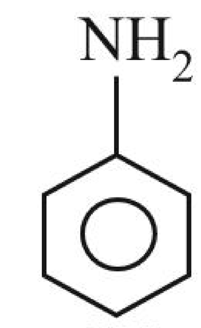
(1) I < IV < II < III (2) IV < II < I < III
(3) I < II < IV < III (4) III < IV < II < I

56. Arrange the following compounds in decreasing order of coupling with benzenediazonium chloride.


I

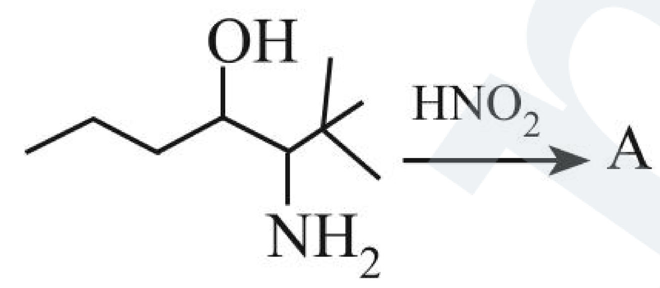

II

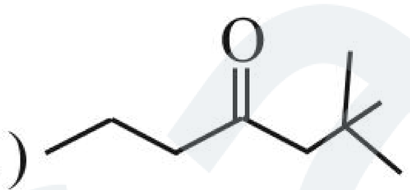
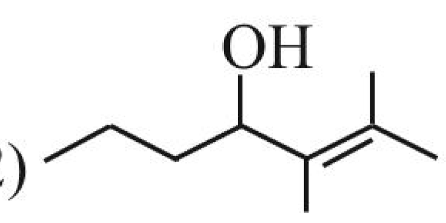

III

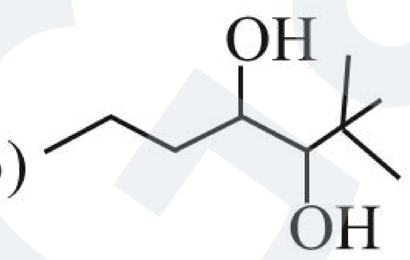
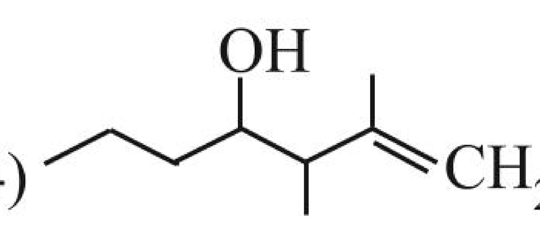

IV

(1) IV > I > II > III (2) II > I > IV > III
(3) II > IV > I > III (4) II > III > IV > I

57. Predict the major product A in the following reaction.

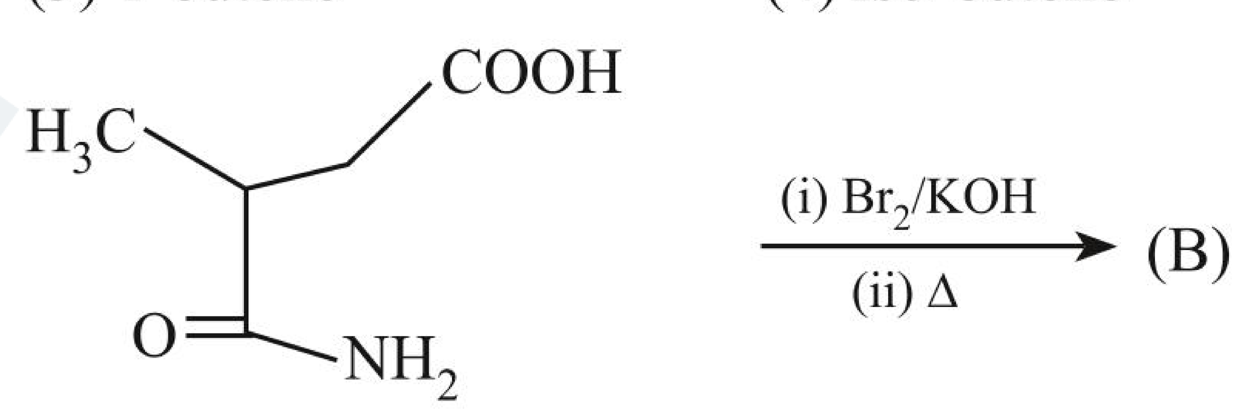


(1)  (2) 

(3)  (4) 

58. Which of the following alkene cannot be prepared by deamination of n-$C_4H_9NH_2$ (Butylamine) with $NaNO_2$/HCl?

(1) *trans*-2-butene (2) *cis*-2-butene
(3) 1-butene (4) *Iso*-butene

59. 

A

The product (B) in the above reaction requence is:

(1) Acrylic acid (2) Crotonic acid
(3) Cinnamic acid (4) Maleic acid

60. $HOCH_2CH_2CN \xrightarrow{H_3O^{\oplus}} B \xrightarrow[\text{(ii) } NH_3]{\text{(i) } SOCl_2} C \xrightarrow{\Delta} D$

In the above reaction requence, the compound (D) is:

(1) Acrylic acid (2) 4-Butyralactam
(3) 4-Methylbutyrolactam (4) δ-Valerolactam

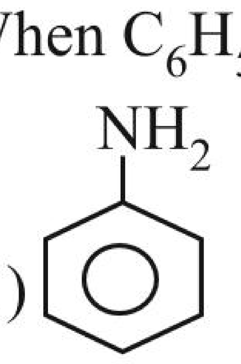
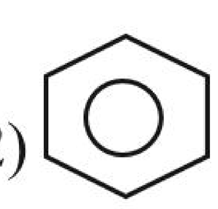
61. The number of isomers including stereoisomers obtained when alanine is heated are:

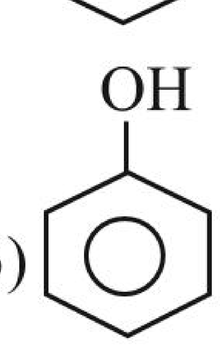
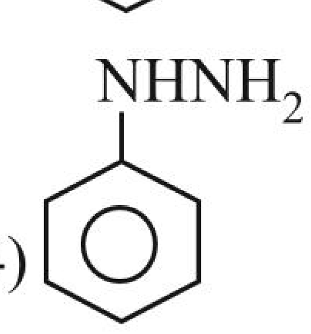
(1) 1 (2) 2
(3) 3 (4) 4

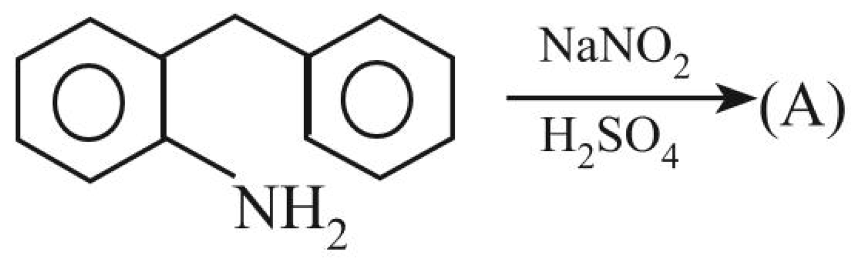
62. Glycine on heating gives:

(1) α,β-unsaturated acid (2) Piperazine
(3) Lactam (4) Polymeric amide

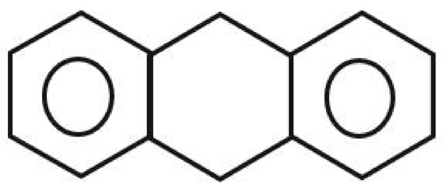
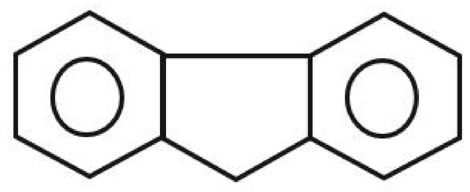
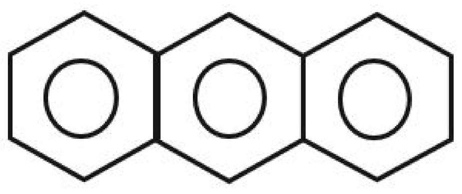
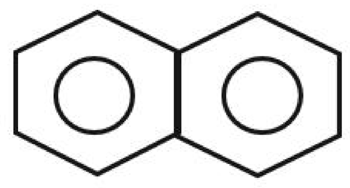
63. When $C_6H_5N_2Cl$ is reduced with Na_2SnO_2, the product is:

(1)  (2) 

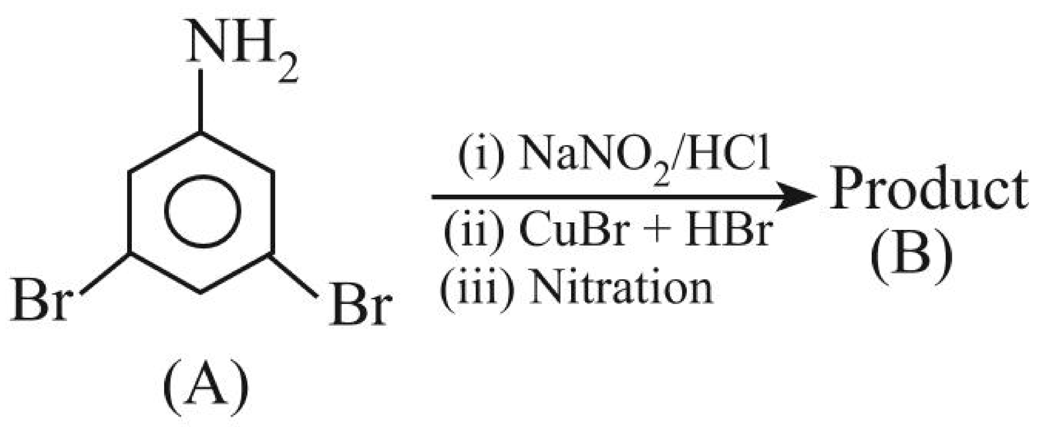
(3)  (4) 

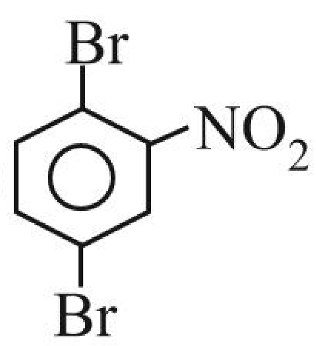
64. 

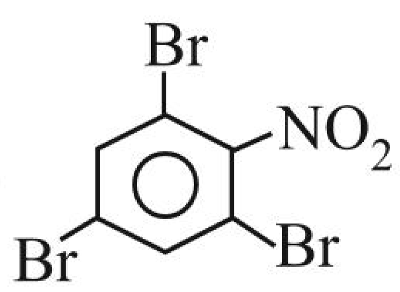
Product of this reaction is:

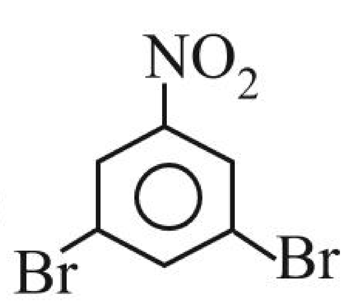
(1) 
(2) 
(3) 
(4) 

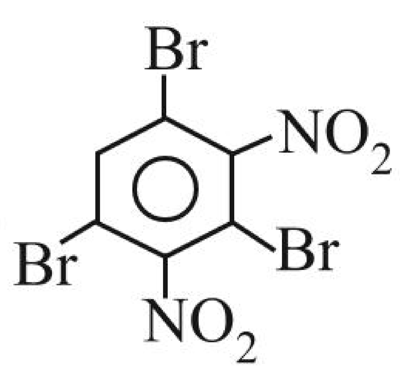
65. Identify the product (B) in the following reaction sequence.

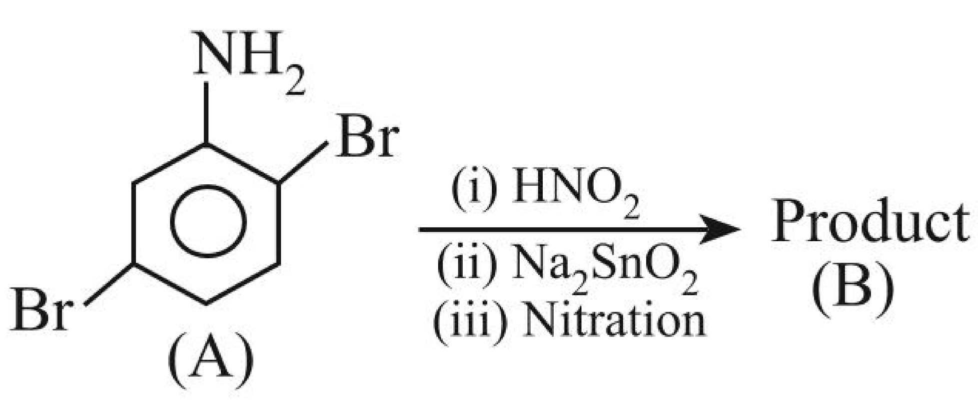


(1) 

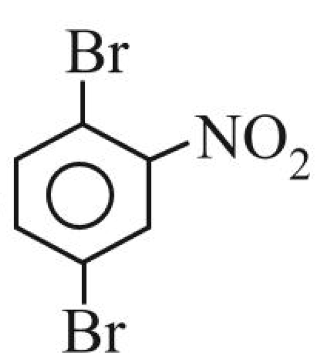
(2) 

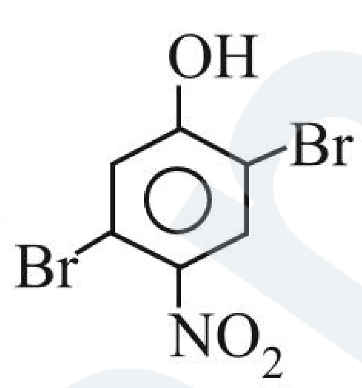
(3) 

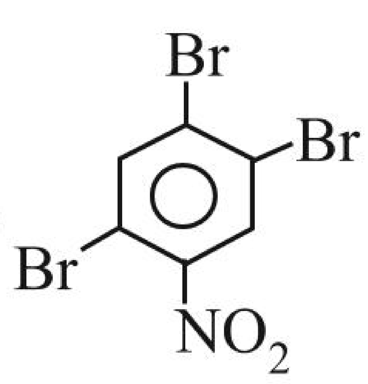
(4) 

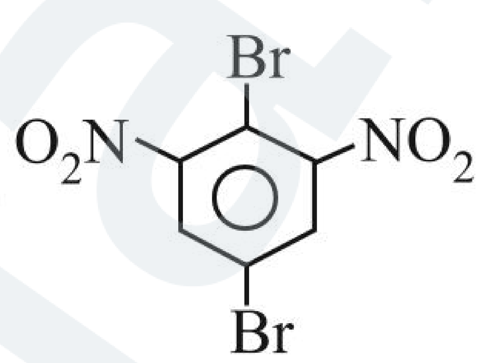
66. 

Identify the product (B) in the above reaction requence.

(1) 

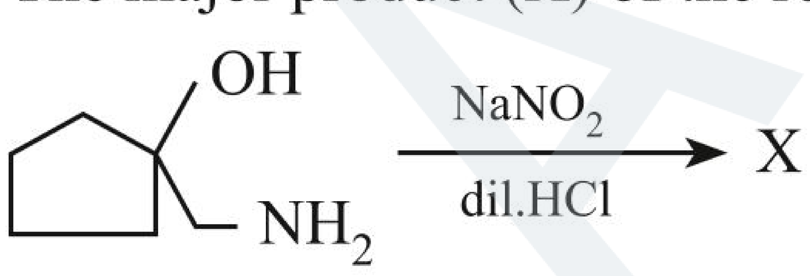
(2) 

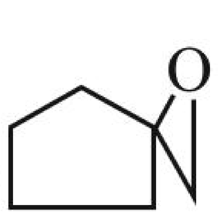
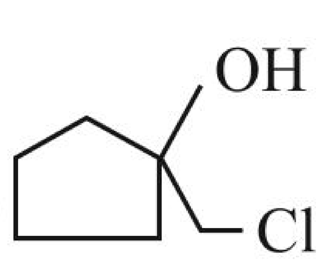
(3) 

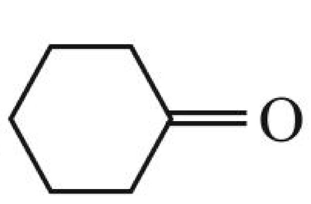
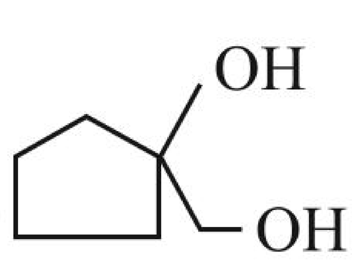
(4) 

Reaction and rearrangement reactions

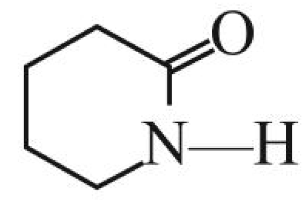
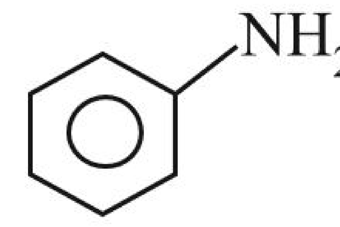
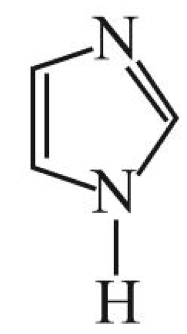
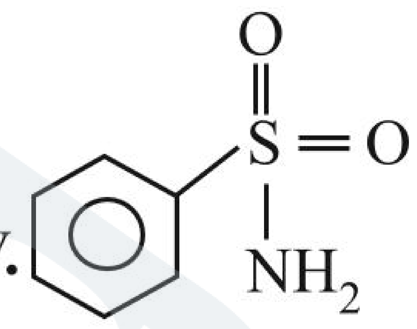
67. The major product (X) of the reaction is:



(1) 
(2) 

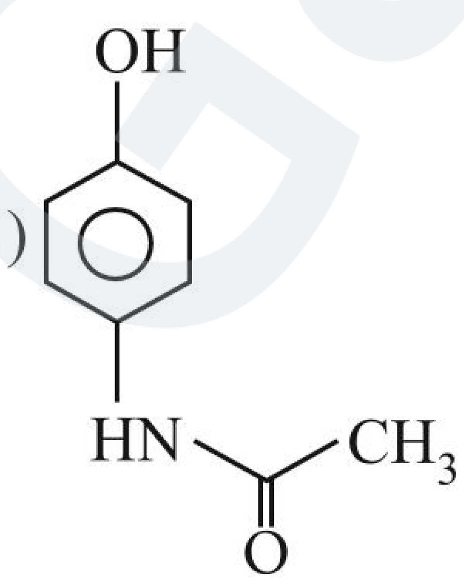
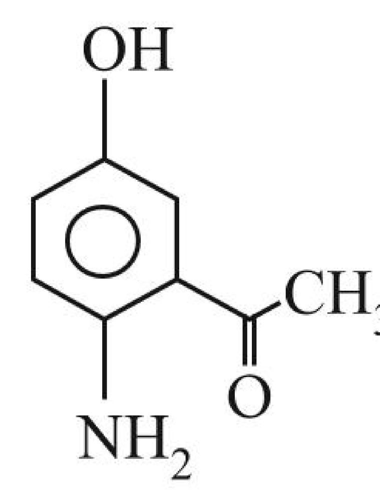
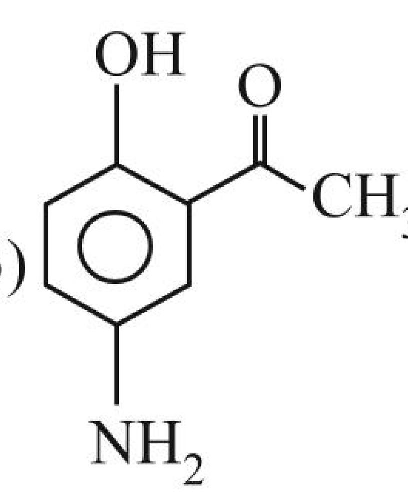
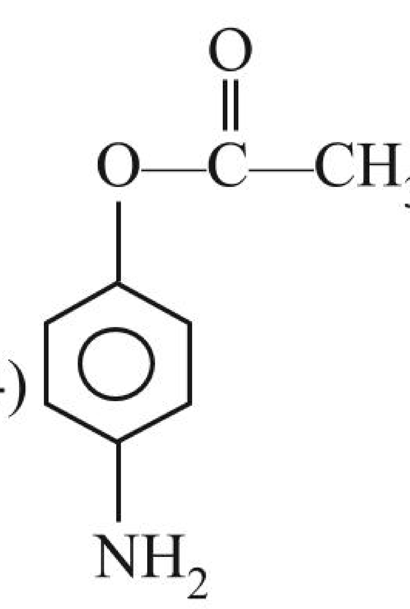
(3) 
(4) 

68. For the following compounds, which is the strongest base and which is strongest acid?

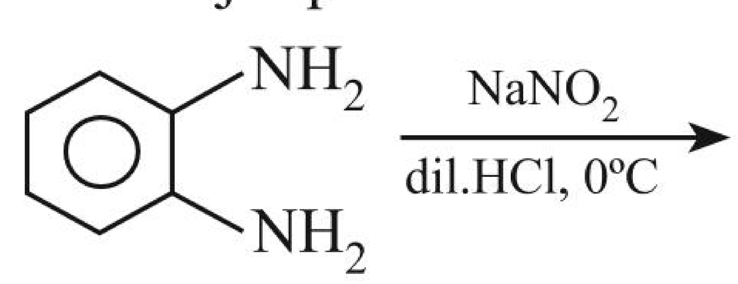
I. 
II. 
III. 
IV. 

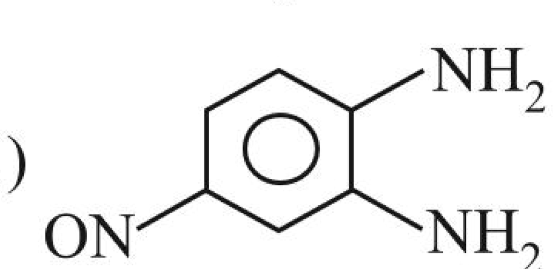
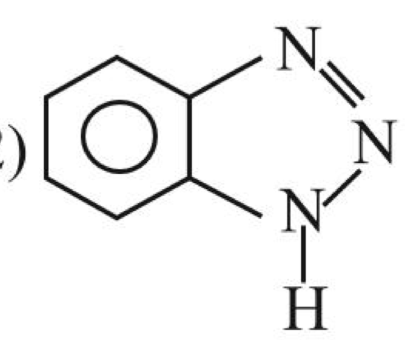
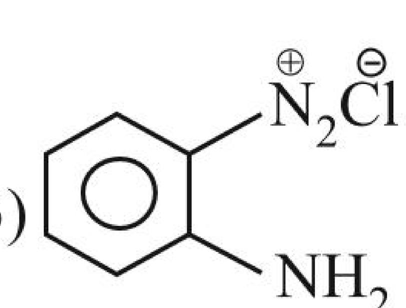
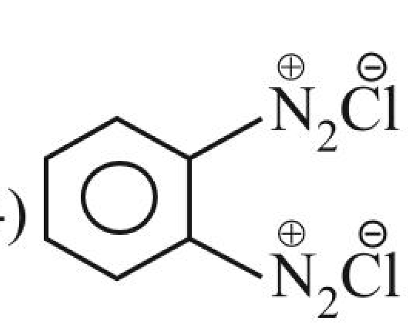
(1) II = Strongest base, III = Strongest acid
(2) III = Strongest base, IV = Strongest acid
(3) IV = Strongest base, III = Strongest acid
(4) II = Strongest base, I = Strongest acid

69. The reaction of *p*-aminophenol with one mole of acetyl chloride in presence of pyridine gives:

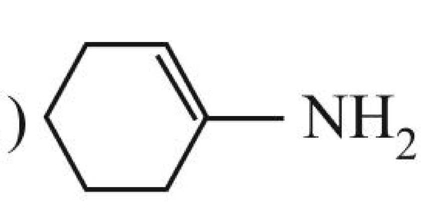
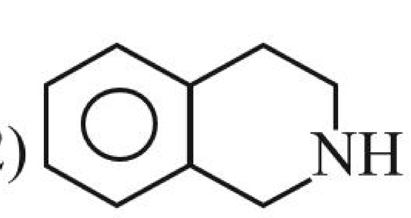
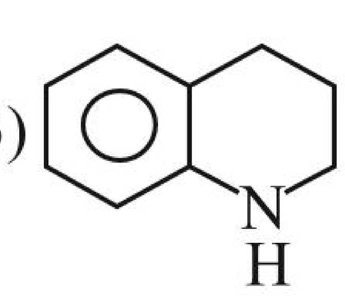
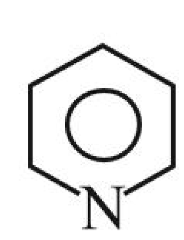
(1) 
(2) 
(3) 
(4) 

70. The major product of the reaction is:

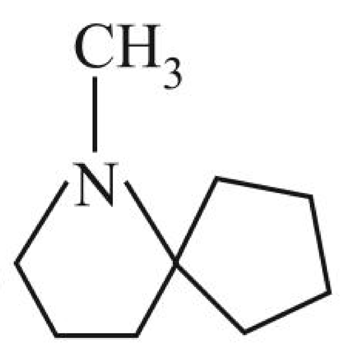


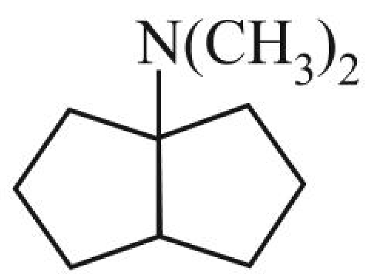
(1) 
(2) 
(3) 
(4) 

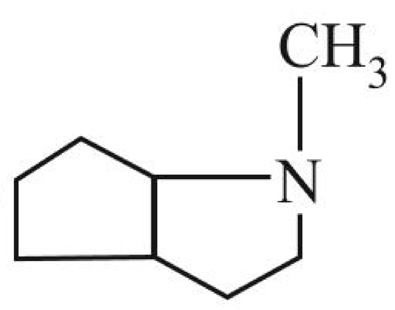
71. Which of the following is most basic?

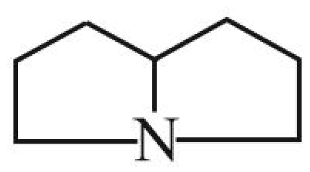
(1) 
(2) 
(3) 
(4) 

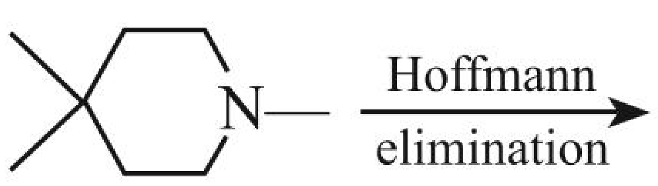
72. Which of the following amines requires the greater number of Hoffmann sequence to accomplish this?

(1) 

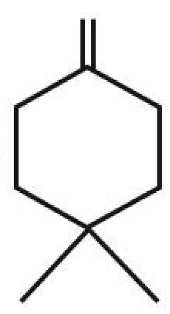
(2) 

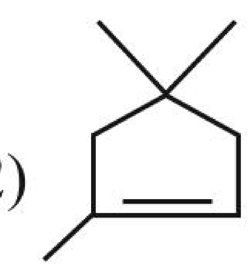
(3) 

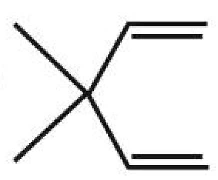
(4) 

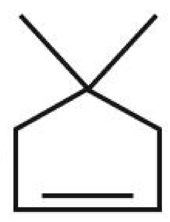
73. 

Product (A). A is:

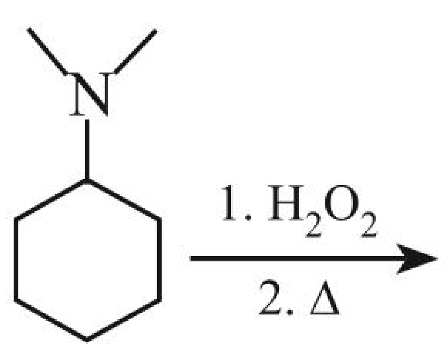
(1) 

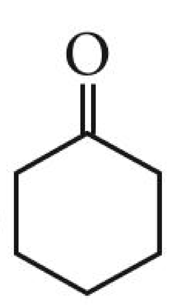
(2) 

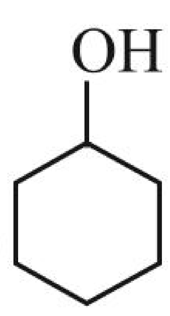
(3) 

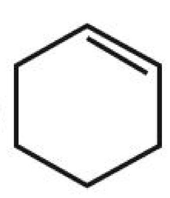
(4) 

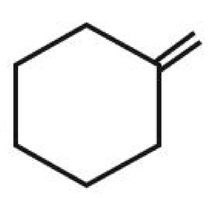
74. What is the likely product from the following reaction?



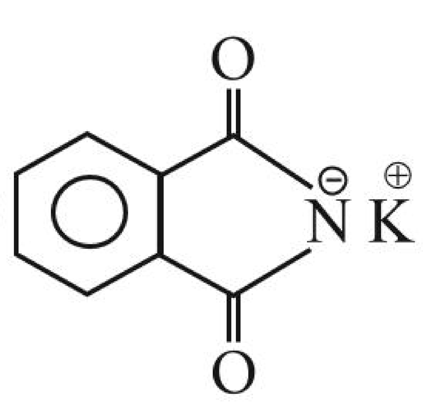
(1) 

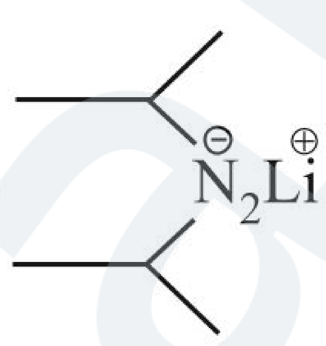
(2) 

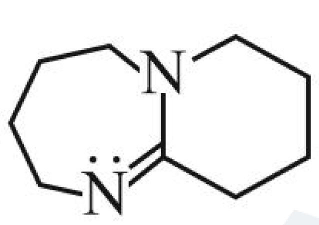
(3) 

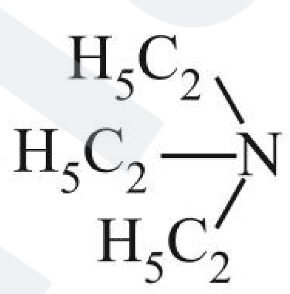
(4) 

75. Which of these is the strongest base?

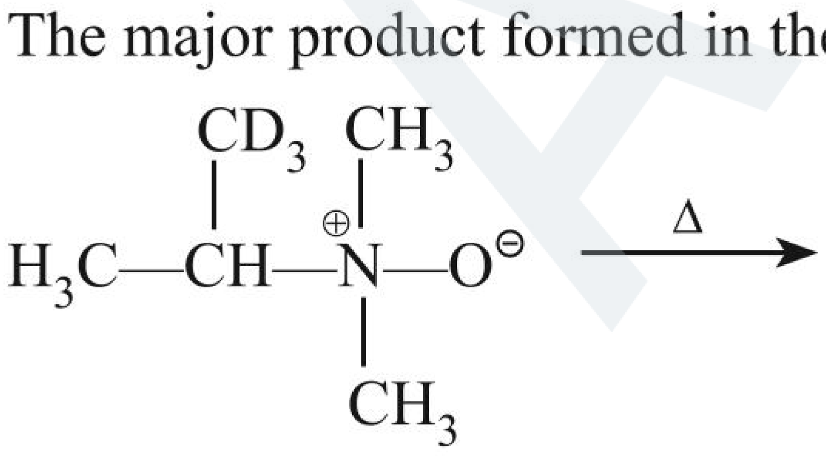
(1) 

(2) 

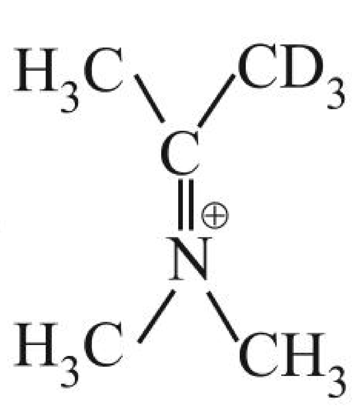
(3) 

(4) 

76. The major product formed in the following reaction is:



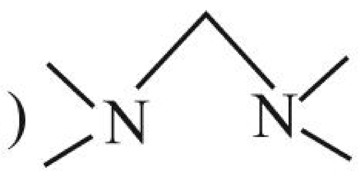
(1) $H_3C—CH=CD_2$

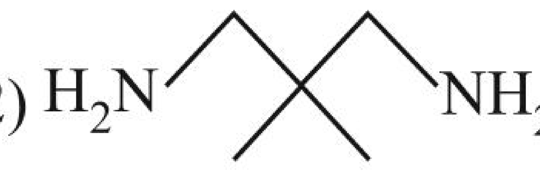
(2) 

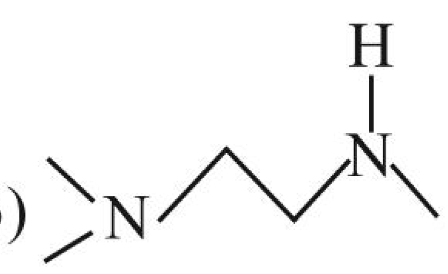
(3) $H_2C=CH—CD_3$

(4) $H_2C=N—CH_3$

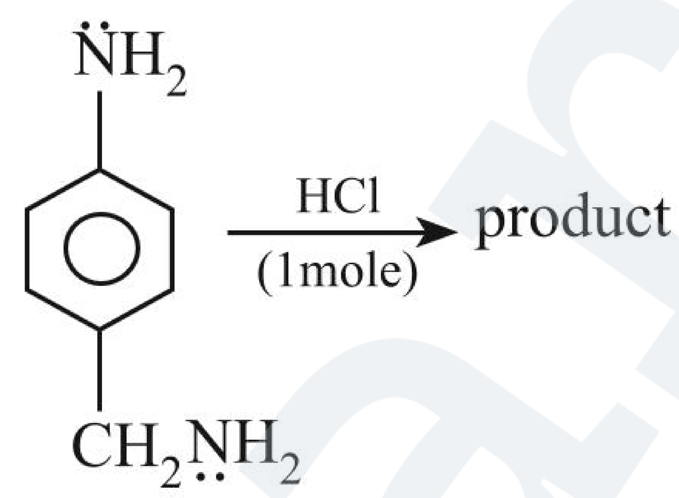
77. The Hinsberg test of a $C_5H_{14}N_2$ compound produces a solid that is insoluble in 10% aq. NaOH. This solid derivative dissolves in 10% aq. H_2SO_4. Which of the following compounds explains above facts?

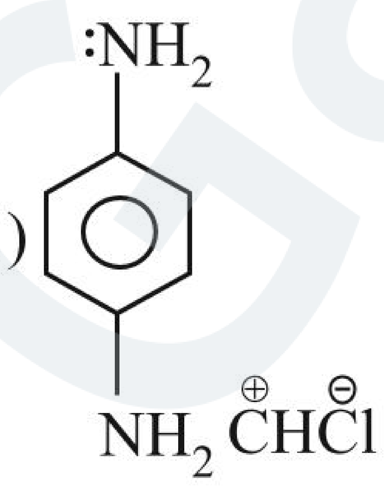
(1) 

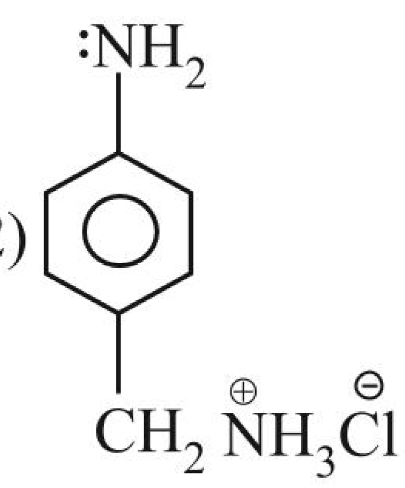
(2) 

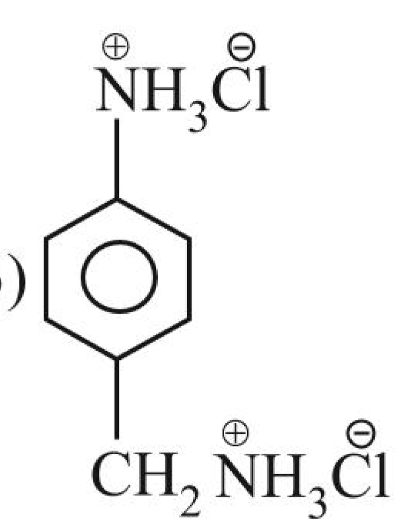
(3) 

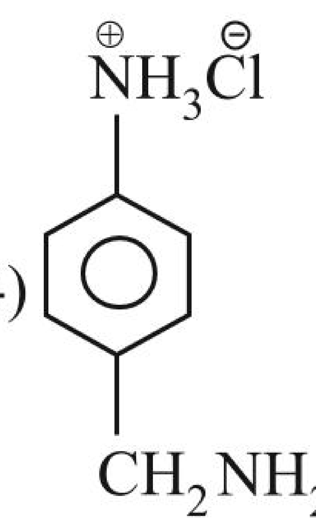
(4) 

78. 

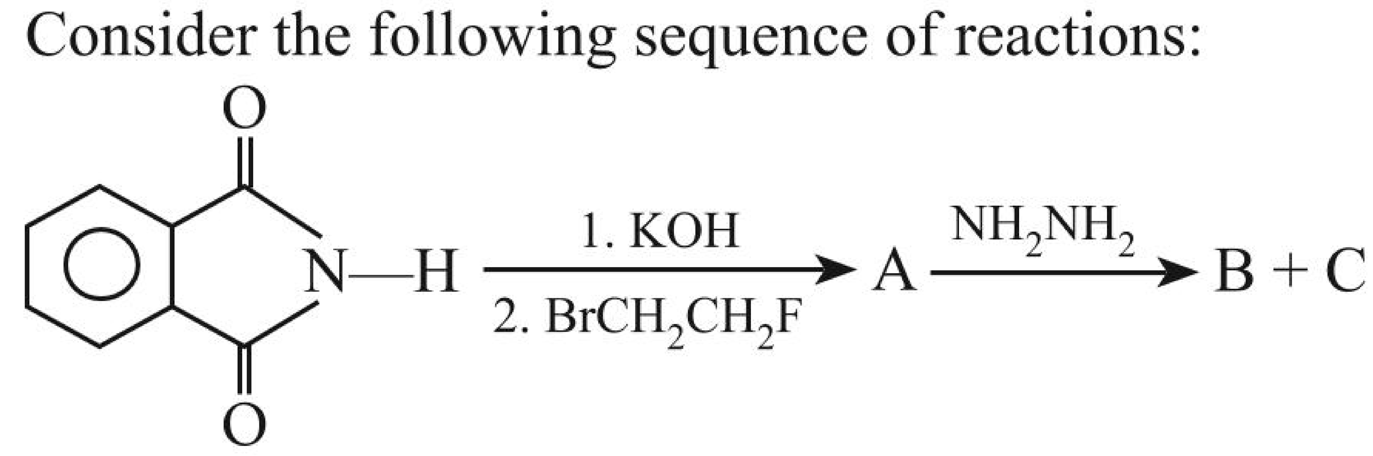
(1) 

(2) 

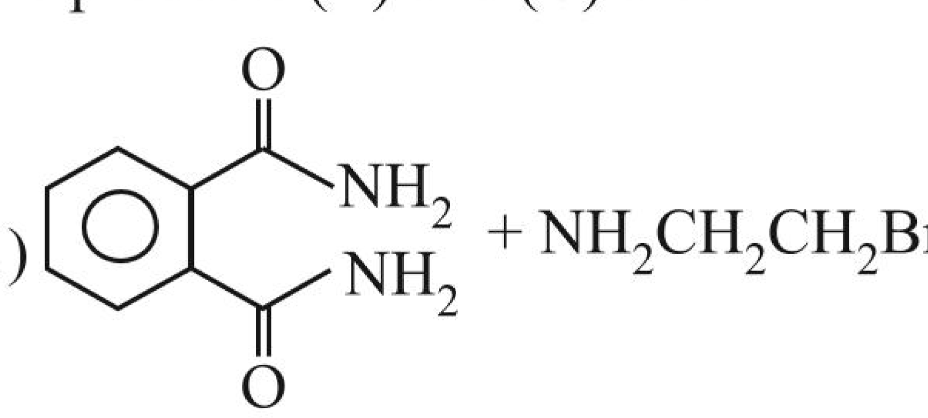
(3) 

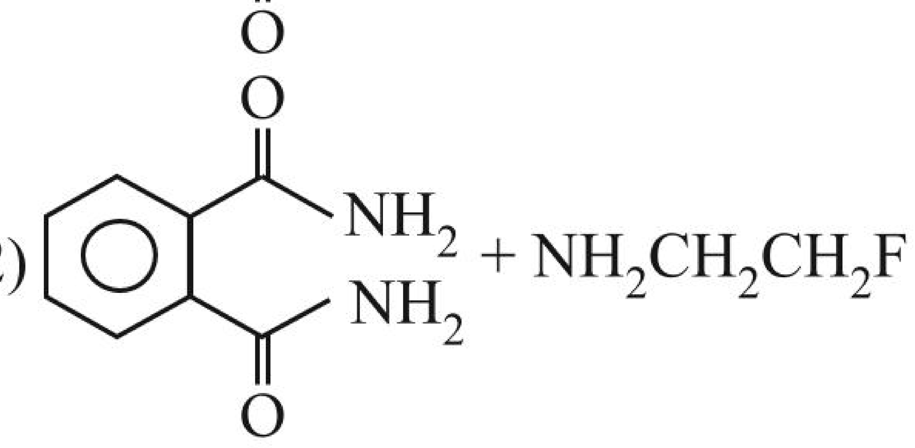
(4) 

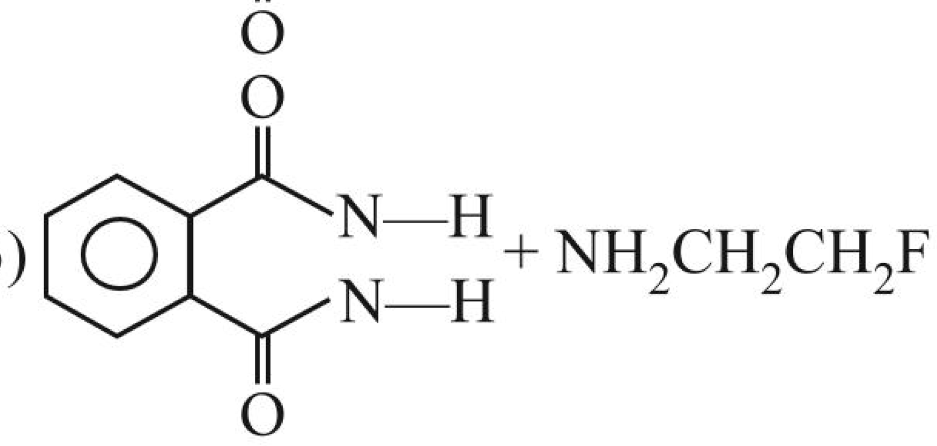
79. Consider the following sequence of reactions:

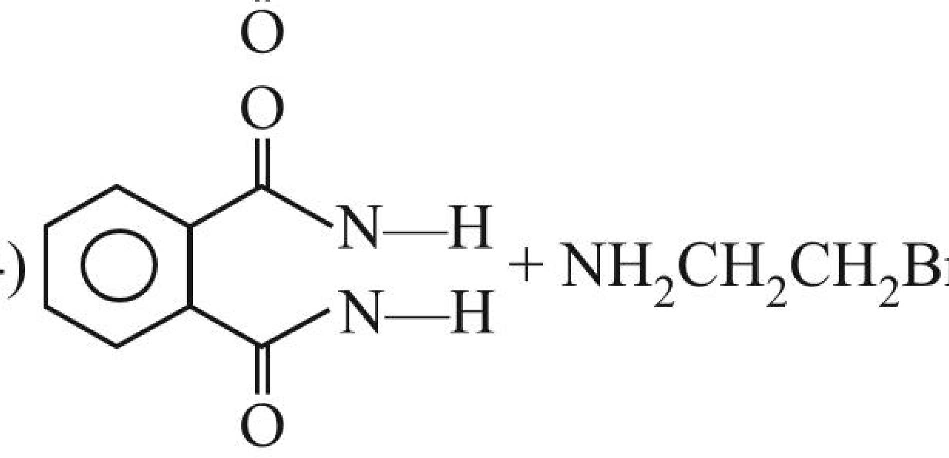


The products (B) and (C) are:

(1) 

(2) 

(3) 

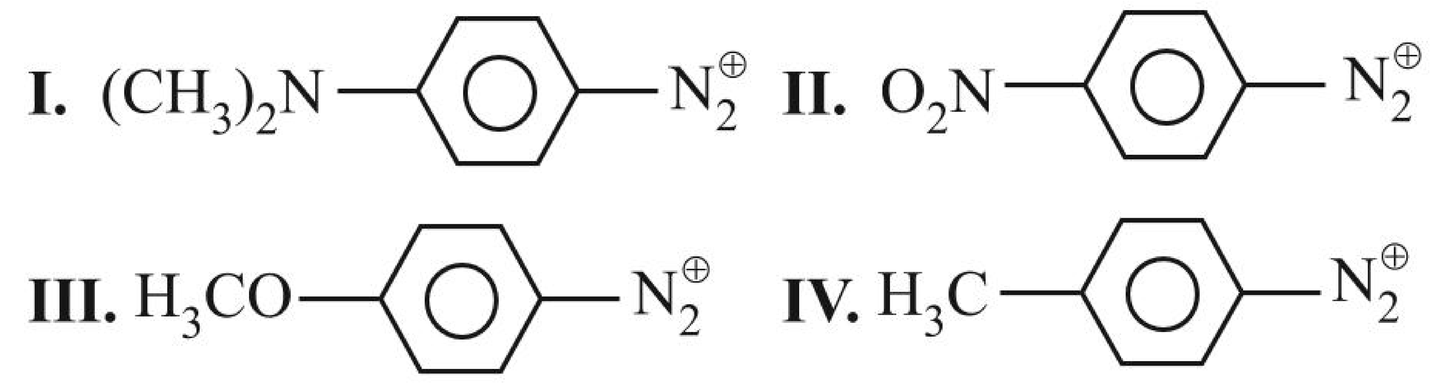
(4) 

80. Identify C in the following sequence of reaction:

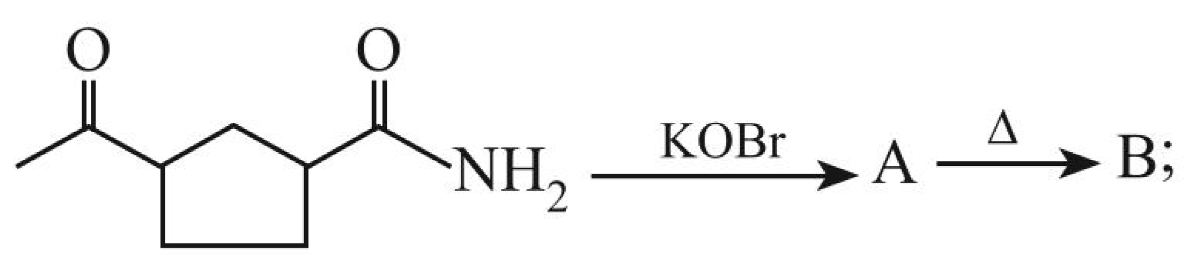
$$Ph\overset{\oplus}{N}\equiv N\overset{\ominus}{Cl}\xrightarrow[KCN]{CuCN}A\xrightarrow{LiAlH_4}B\xrightarrow{HNO_2}C$$

(1) Benzamide (2) Phenyl acetic acid
(3) Benzyl alcohol (4) Benzoic acid

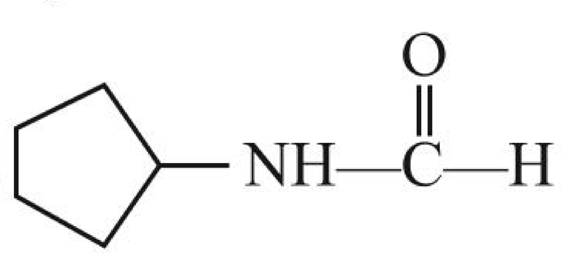
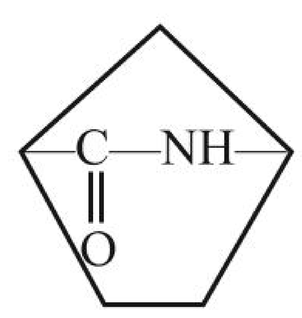
81. The order of reactivity towards diazo coupling with phenol in presence of dil. NaOH:

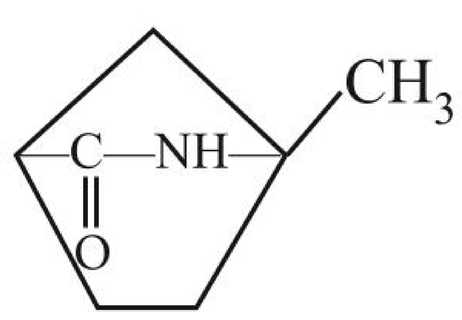
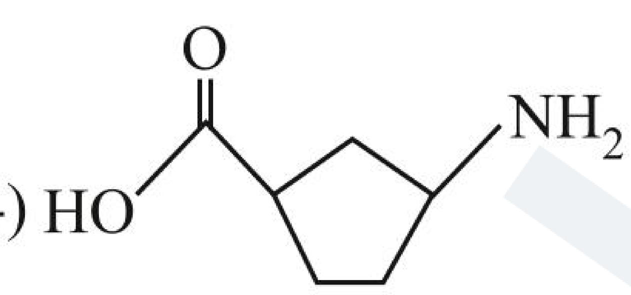


(1) I > II > III > IV (2) II > IV > III > I
(3) I > III > IV > I (4) IV > III > II > I

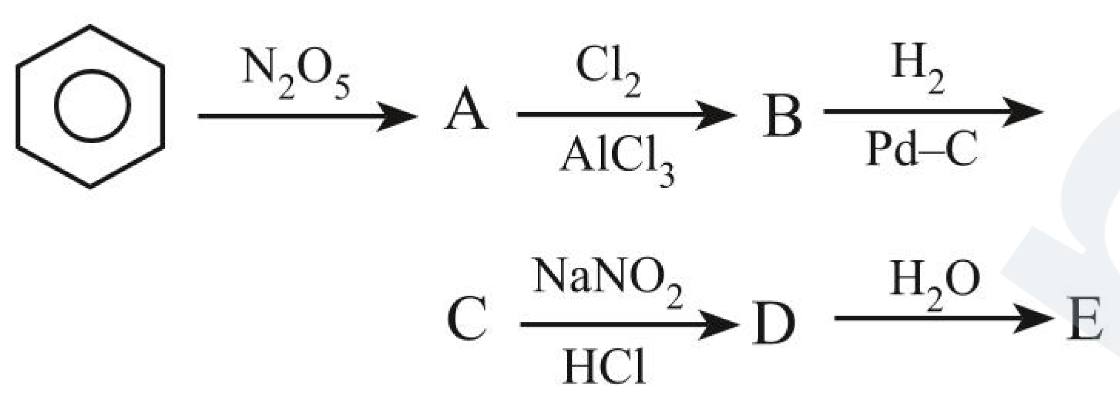
82. 

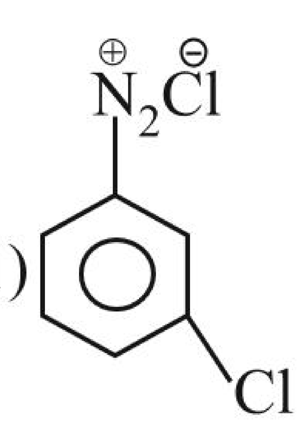
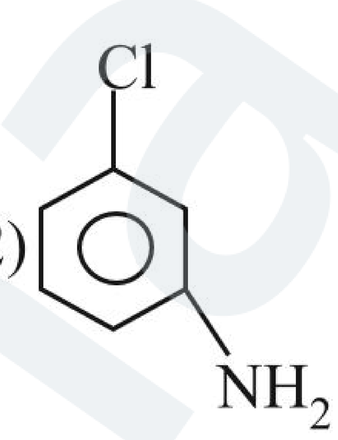
Compound B is:

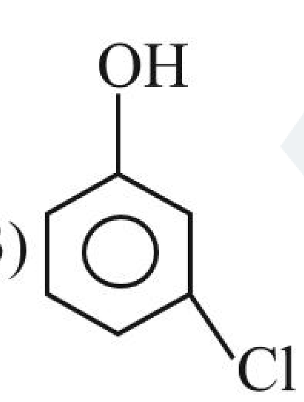
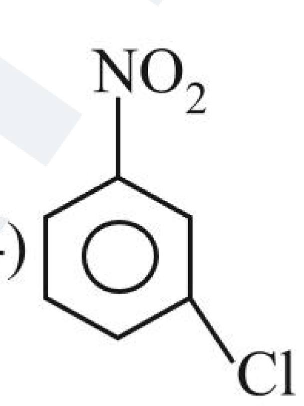
(1)  (2) 

(3)  (4) 

83. Identify the final product (E) of following sequence of reaction:



(1)  (2) 

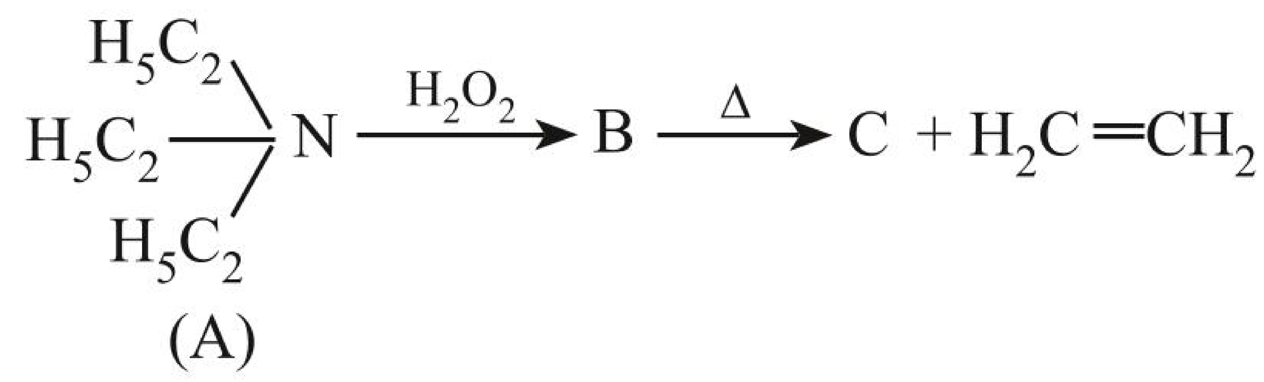
(3)  (4) 

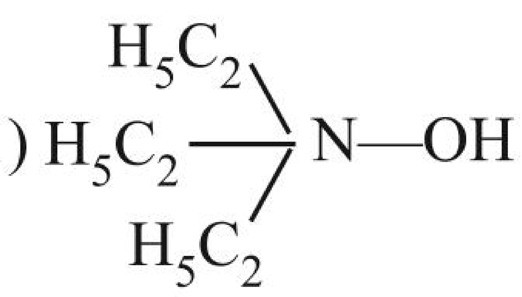
84. $\underset{(A)}{C_2H_5COOH}\xrightarrow{SOCl_2}(B)\xrightarrow{NH_3}(C)\xrightarrow[Br_2]{KOH}(D)$

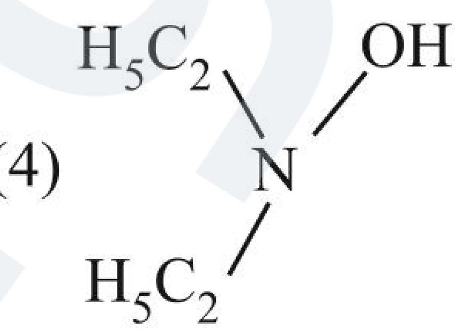
Compound (D) is:

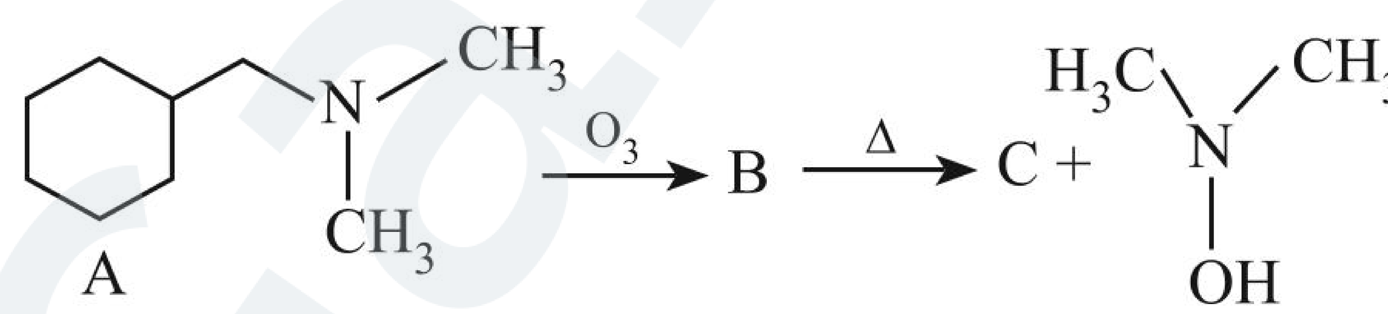
(1) $C_2H_5NHCH_3$ (2) $C_2H_5NH_2$
(3) $C_3H_7NH_2$ (4) $C_2H_5CONH_2$

85. The final product C obtained in the reaction is:

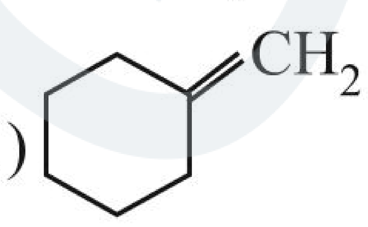
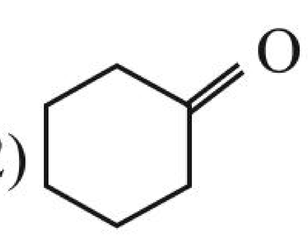


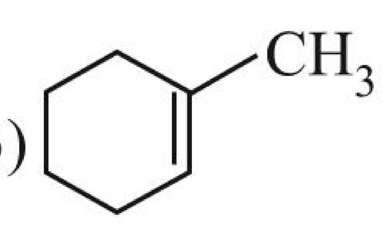
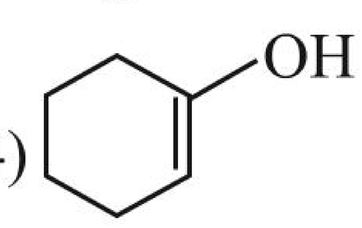
(1)  (2) $(H_2C=CH_2)_2$

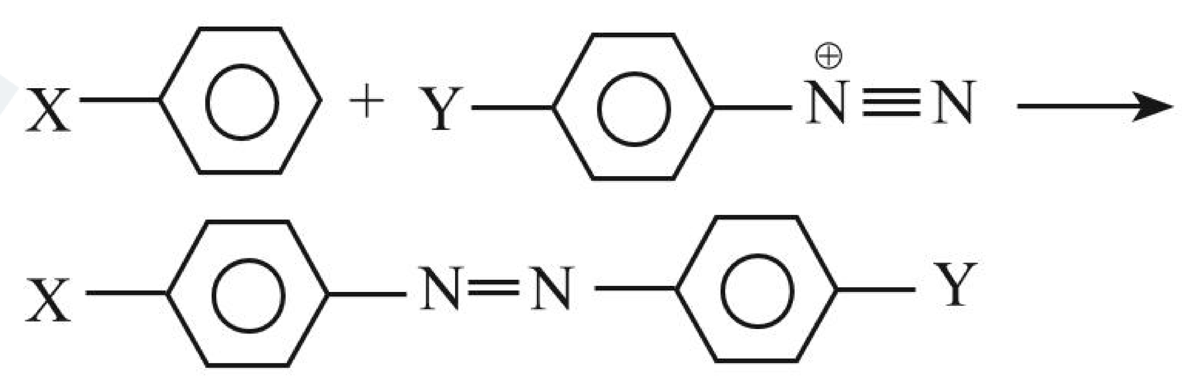
(3) $H_3C-CH=CH_2$ (4) 

86. 

Identify 'C':

(1)  (2) 

(3)  (4) 

87. 

For such kind of diazo-coupling reaction the suitable substituents X and Y are respectively :

(1) $-OCH_3$ and $-N\overset{\nearrow O}{\searrow O}$ (2) $-NO_2$ and $-\overset{O}{\overset{\|}{C}}-H$

(3) $-NH_2$ and $-NHCH_3$ (4) $-NH_2$ and $-OCH_3$

88. A compound 'A' when reacted with PCl_5 and then with NH_3 gives 'B'. When 'B' is treated with Br_2 and KOH produced 'C'. C on treatment with $NaNO_2$ + HCl at 0ºC and then boiling produced *ortho*-cresol. Compound 'A' is :

(1) *m*-Toluic acid (2) *o*-Chlorotoluene
(3) *o*-Bromotoluene (4) *o*-Toluic acid

89. 1º, 2º and 3º nitroalkane can be identified by action of :

(1) $CHCl_3$ + KOH (alc.) (2) $CHCl_3$ + NaOH (aq.)
(3) HNO_2 + NaOH (aq.) (4) HNO_3 + NaOH (aq.)

Cyanides Isocyanides and Nitro Compounds

90. Which statement is wrong about the hydrolysis of $R-\overset{\oplus}{N}\equiv\overset{\ominus}{C}$?

(1) Isocyanides are hydrolysed with aqueous dilute acids but not by alkali.

(2) In the hydrolysis of $(R-\overset{\oplus}{N}\equiv\overset{\ominus}{C})$, first electrophile $(H^{\oplus})$ add on the C atom and then nucleophile $(\overset{\ominus}{O}H)$ adds to the same C atom.

(3) On partial hydrolysis, (RNC) gives N-substituted methanamide or formamide.
(4) On complete hydrolysis, (RNC) gives 1° amine and RCOOH.

91. $R-\overset{\overset{O}{\|}}{C}-\overset{\ominus}{C}H-\overset{\oplus}{N}\equiv\ddot{N} \longrightarrow$ Intermediate + N_2

What is the nature of intermediate in this reaction?

(1) Carbonium ion (2) Carbanion
(3) Carbene (4) Free radical

92. The order of increasing boiling points among the three compounds is:

C_2H_5ONO (I) $C_2H_5NO_2$ (II) C_2H_6 (III)

(1) III < II < I (2) I < II < III
(3) III < I < II (4) III < I ≈ II

93. When a 2° aromatic amine hydrochloride is heated, it leads to the formation of 1° amine hydrochloride. The reaction is known as:

(1) Hoffmann degradation
(2) Fries migration
(3) Hoffmann Martius rearrangement
(4) None of these

94. In Hoffmann bromamide degradation, one of the important steps is the migration of :

(1) An alkyl group without its electron pair to electron deficient N atom.
(2) An alkyl group with its electron pair to electron deficient O atom.
(3) An alkyl group with its electron pair to electron rich N atom.
(4) An alkyl group with its electron pair to electron deficient N atom.

95. The product (C) in the following reaction is:

$\underset{(A)}{C_2H_5Cl} \xrightarrow{AgCN} (B) \xrightarrow[DMSO]{Cl_2^{\oplus}} (C)$

(1) C_2H_5COOH (2) C_2H_5NCO
(3) C_2H_5COCl (4) $ClCH_2CH_2NCO$

96. Select the incorrect statement.

(1) 1° nitro compound with HNO_2 gives nitrolic acid, which gives blood red colour with base.
(2) 2° nitro compound with HNO_2 gives pseudo nitrole, which gives blue colour with base.
(3) 3° nitro compound reacts with HNO_2 which gives yellow colour with base.
(4) 1° aliphatic amine with HNO_2 liberates N_2 gas.

97. The product (B) and (C) in the following reaction:

$\underset{(A)}{C_6H_5NO_2}$ $\xrightarrow{LAH}$ (B)

$\underset{(A)}{C_6H_5NO_2}$ $\xrightarrow{Al\text{-}Hg/H_2O}$ (C)

(B)	(C)
(1) Aniline	Azoxybenzene
(2) Azoxybenzene	Aniline
(3) Azobenzene	Hydrazobenzene
(4) Hydrazobenzene	Azobenzene

98. $\underset{(A)}{\text{Benzene}} \xrightarrow[+\ H_2SO_4]{HNO_3} (B) \xrightarrow[+\ NaOH]{Na_2SnO_2} (C)$

$(B) \xrightarrow[+\ NaOH]{Na_3AsO_3} (D)$

The product **(C)** and **(D)** in the above reaction are

(C)	(D)
(1) Azobenzene	Azoxybenzene
(2) Azoxybenzene	Azobenzene
(3) Aniline	Hydrazobenzene
(4) Hydrazobenzene	Aniline

99. $\underset{A}{C_2H_5Cl} \xrightarrow{AgCN} B \xrightarrow[H_3O^{\oplus}]{Partial} C \xrightarrow{H_2O} C_2H_5NH_2 + D$

Select the correct statement from the above reaction sequence:

(1) The compound (C) is N-ethylmethanamide and (D) is HCOOH.
(2) The compound (C) is N-methylmethanamide and (D) is HCOOH.
(3) The compound (C) is N-ethylmethanamide and (D) is CH_3COOH.
(4) The Compound (C) is N-methylmethanamide and (D) is CH_3COOH.

100. An amine on treatment with HNO_2 evolved N_2. The amine on exhaustive methylation with CH_3I formed a quaternary salt containing 59.07% iodine. The amine is likely to be :

(1) CH_3NH_2 (2) $(CH_3)_2NH$
(3) $C_2H_5NH_2$ (4) $(CH_3)_3N$

101. A compound (X) has the molecular formula C_3H_7NO. With Br_2 and KOH, (X) gives (Y).(Y) responds to mustard oil reaction. (Y) upon treatment with HNO_2 evolves N_2 and gives an alcohol (Z) which gives iodoform test. (X) is likely to be :

(1) $C_2H_5CONH_2$ (2) CH_3CONH_2
(3) CH_3COONH_4 (4) C_2H_5CNO

102. A compound (X) has the molecular formula C_7H_7NO. On treatment with Br_2 and KOH, (X) gives an amine (Y) ; (Y) gives carbylamine test. (Y) upon diazotisation and coupling with phenol gives an azo dye (Z). (X) is:

(1) $PhCONH_2$ (2) $PhCONHCOCH_3$
(3) $PhNO_2$ (4) $PhCOONH_4$

103. Which of the following substances on treatment with P_2O_5 gives ethanenitrile?

(1) Propanamide (2) Ethanamide
(3) Ethanoic acid (4) *N*-Methylethyl amine

104. Methyl cyanide on treatment with methyl magnesium bromide followed by of subsequent hydrolysis gives:

(1) Propanone (2) Ethanone
(3) Ethanal (4) Propanal

105. The product formed by the treatment of ethanol and ethane nitrile in the presence of sulphuric acid is:

(1) Ethyl acetate (2) Diethyl ether
(3) Ethyl methyl ketone (4) Butanal

106. Which of the following reagents on treatment with benzenamine in basic medium produces phenyl isocyanide?
(1) CCl_4 (2) Trichloromethane
(3) Methylene dichloride (4) Hexachloroethane

107. (A) is subjected to reduction with Zn–Hg/HCl and the product formed is *N*-methylmethanamine. (A) can be:
(1) Ethane nitrile (2) Nitroethane
(3) Carbylaminoethane (4) Carbylaminomethane

108. When propane is subjected to the treatment with fuming nitric acid at 673 K, which of the following will not be formed?
(1) 1-Nitropropane (2) 2-Nitropropane
(3) Nitromethane (4) Nitrohexane

109. Nitrobenzene is subjected to reduction with zinc dust and ammonium chloride. The main product formed will be:
(1) Benzenamine (2) Aniline
(3) *N*-Phenylhydroxylamine (4) None of these

110. A primary nitroalkane is treated with nitrous acid, which of the following will be the main product?
(1) Pseudonitrol (2) Nitrolic acid
(3) A primary amine (4) Primary alcohol

111. Nitromethane is subjected to treatment with chlorine in the presence of sodium hydroxide, the main product is:
(1) Monochloronitromethane
(2) Trichloromethane
(3) Chloropicrin
(4) None of the above

112. A nitrogenous substance (X) is treated with HNO_2 and the product so formed is further treated with NaOH solution, which produces blue colouration. Which of the following can (X) be?
(1) $CH_3CH_2NH_2$ (2) $CH_3CH_2NO_2$
(3) CH_3CH_2ONO (4) $(CH_3)_2CHNO_2$

113. An organic compound with the formula C_3H_5N on hydrolysis forms an acid which reduces Fehling's solution. The compound can be:
(1) Ethanenitrile (2) Isocyanoethane
(3) Ethoxyethane (4) Propanenitrile

114. Which of the following represents the poisonous gas which caused the tragedy in Bhopal in 1984?
(1) $CH_3C{=}N{=}S$ (2) $CH_3{-}N{=}C{=}O$
(3) $CH_3{-}N{=}C{=}S$ (4) $CH_3{-}O{-}N{=}C$

115. The product of the reaction of alcoholic silver nitrite with ethyl bromide is:
(1) Ethane (2) Ethene
(3) Nitroethane (4) Ethyl alcohol
(5) Ethyl nitrite

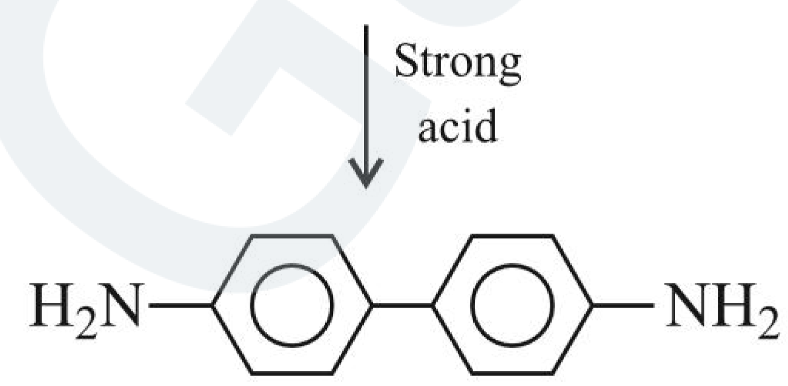
116. The electrolytic reduction of nitrobenzene in strongly acidic medium produces:
(1) Phenol (2) *p*-Aminophenol
(3) Hydroazobenzene (4) Azobenzene

117. Azoxybenzene can be obtained by the treatment of nitrobenzene with:
(1) O_2 (2) H_2/Pt
(3) $Na_3AsO_3/NaOH$ (4) Zn/NaOH

118. Tertiary nitro compounds cannot show tautomerism because:
(1) They are very stable.
(2) They isomerise to give secondary nitro compounds.
(3) They do not have labile hydrogen atom.
(4) They are highly reactive.

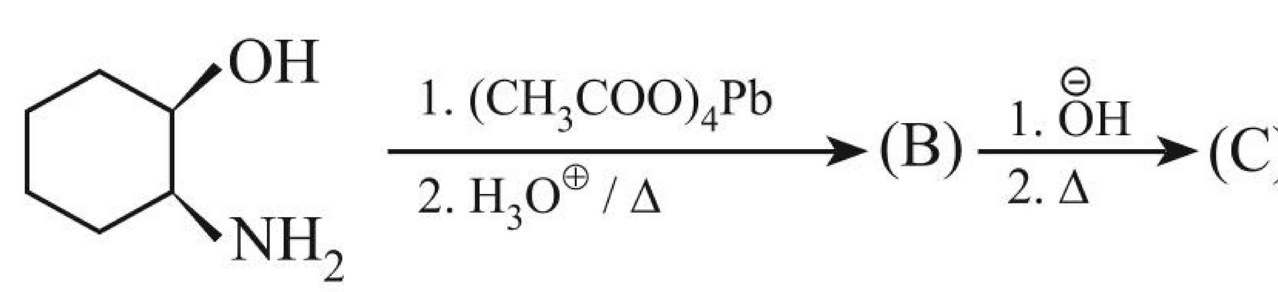
119. When $PhNO_2$ is reduced in alkaline medium, the product is:
(1) $Ph{-}\overset{\overset{O}{\uparrow}}{N}{=}N{-}N{-}Ph$ (Azoxy-benzene)
(2) Ph—N═N—Ph (Azobenzene)
(3) Ph—NH—NH—Ph (Hydrazobenzene)
(4) All

120. The following reaction is:
Ph—NH—NH—Ph



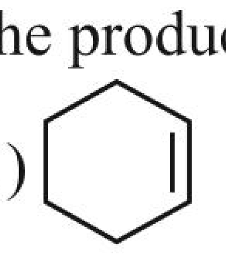
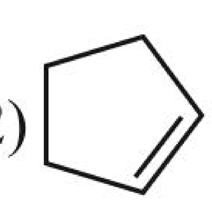
(1) Benzidine rearrangement
(2) Pinacol–Pinacolone rearrangement
(3) Fries rearrangement
(4) Benzil–benzilic acid arrangement

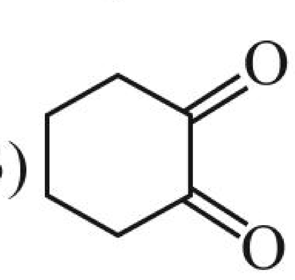
Miscellaneous

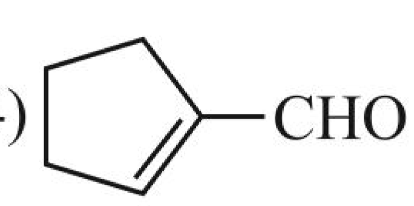
121. 

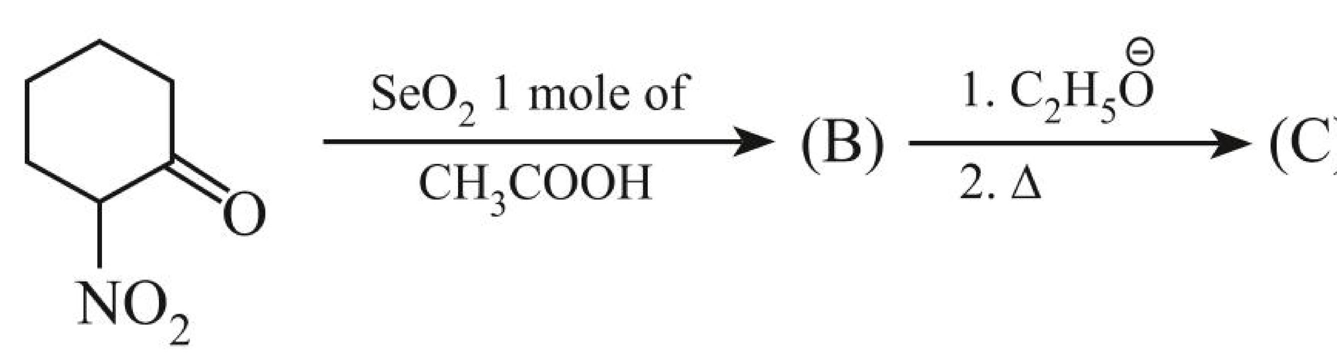
(A)

The product (C) is:

(1)  (2) 

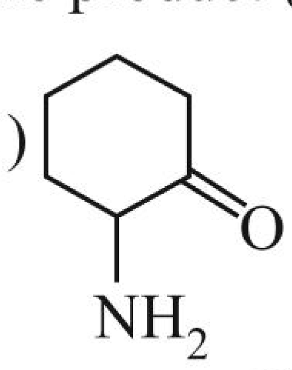
(3) 

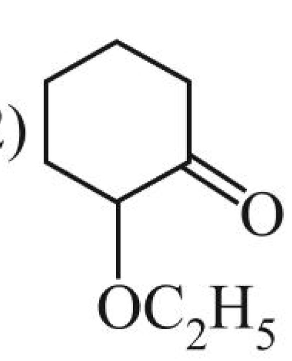
(4) 

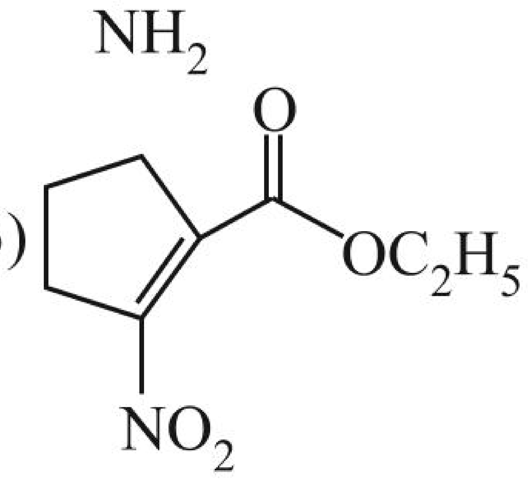
122. 

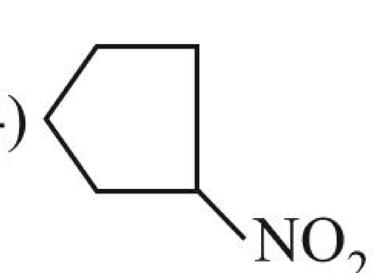
(A)

The product (C) is:

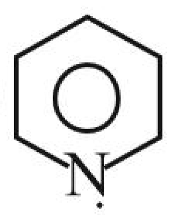
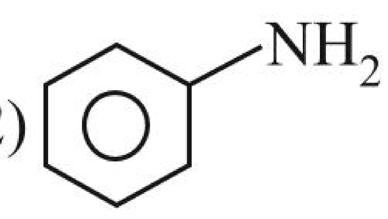
(1) 

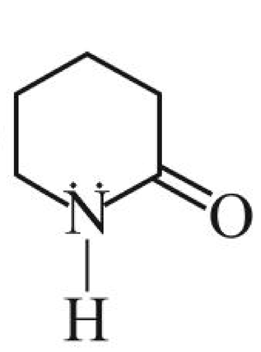
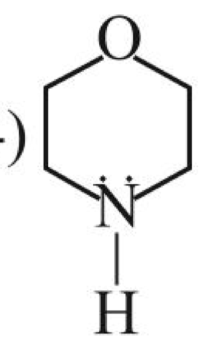
(2) 

(3) 

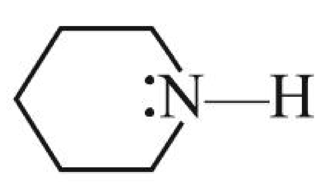
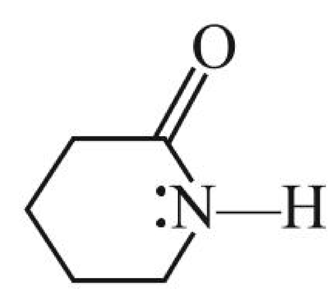
(4) 

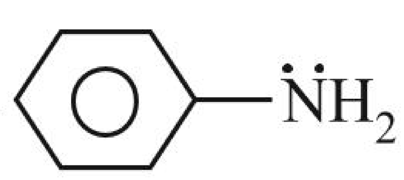
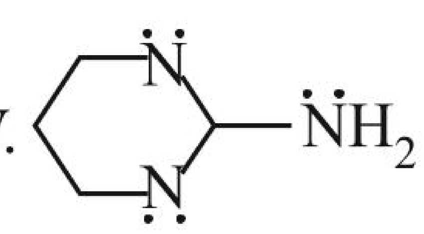
123. Which of the following will react with cyclo pentanone to form an enamine?

(1)  (2) 

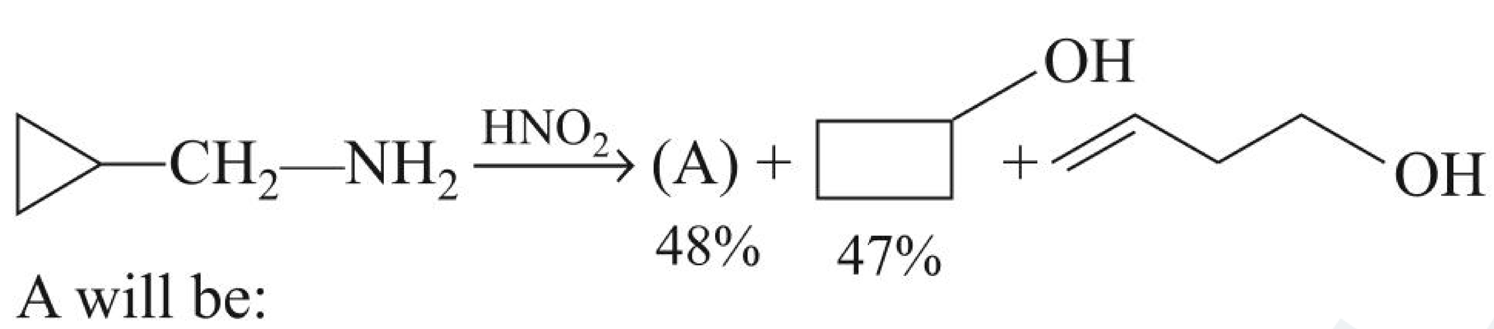
(3)  (4) 

124. Which of the following are strongest Brnosted acid and strongest Brnosted base respectively.

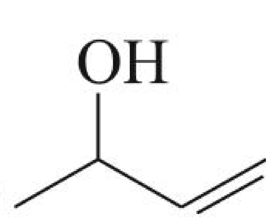
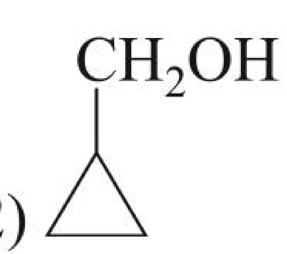
I.  II. 

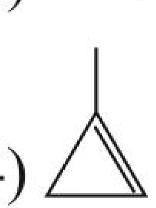
III.  IV. 

(1) I and II (2) I and III
(3) II and III (4) II and IV

125. 

A will be:

(1)  (2) 

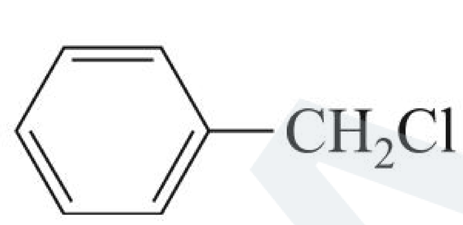
(3)  (4) 

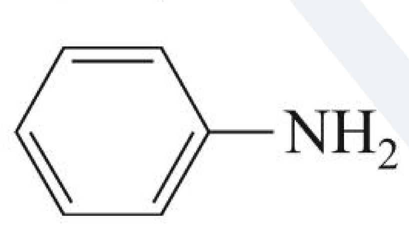
126. Which of the following arylamines will not form a diazonium salt on reaction with sodium nitrite in hydrochloric acid?

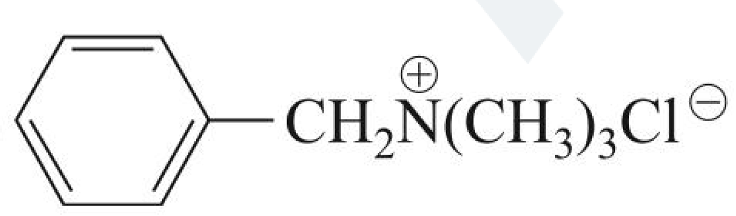
(1) *m*-Ethylaniline
(2) *p*-Aminoacetophenone
(3) 4-Chloro-2-nitroaniline
(4) *N*-Ethyl-2-methylaniline

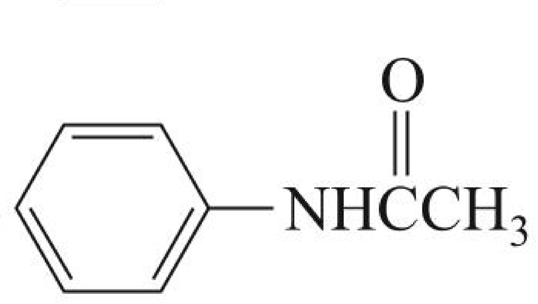
127. Which one of the following is best catalyst for the reaction shown below?

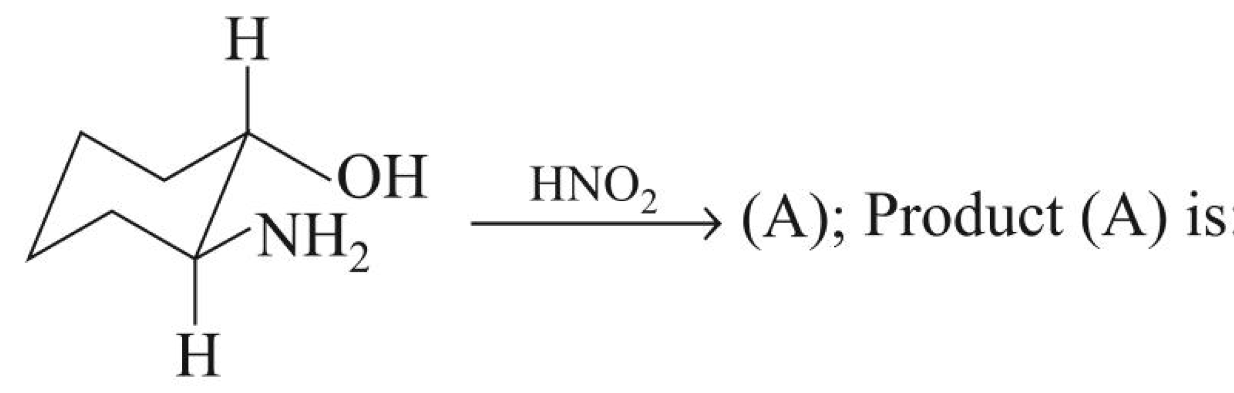
$CH_3(CH_2)_8CH_2Br \xrightarrow[\text{benzene}]{\text{KCN}} CH_3(CH_2)_8CH_2CN$

(1) 

(2) 

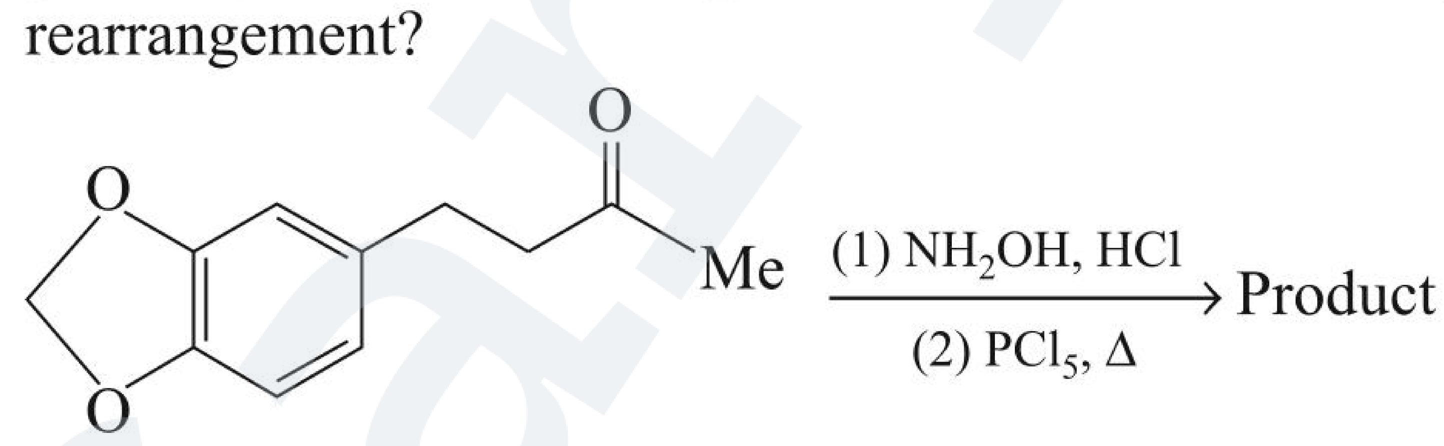
(3) 

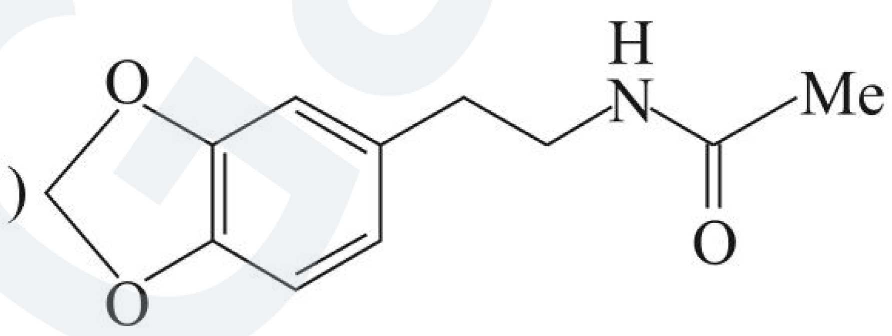
(4) 

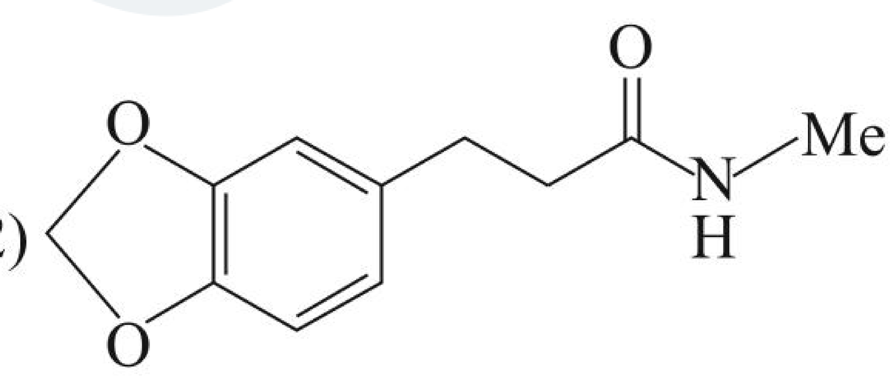
128. 

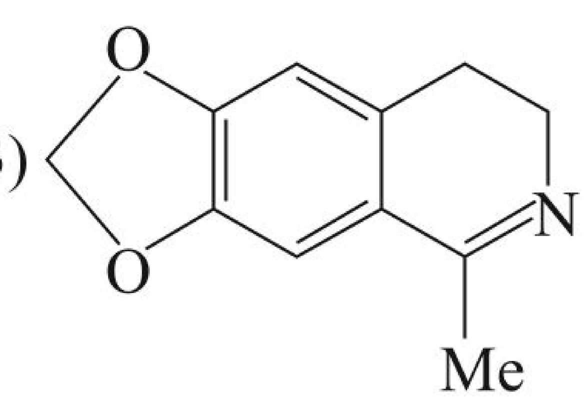
(1) cyclohexane-1, 2-diol
(2) 2-aminocyclohexene
(3) cyclopentane carboxyaldehyde
(4) cyclohex-2enol

129. Which of the following product will be obtained in the given (consider minor product also) Beckmann-type rearrangement?

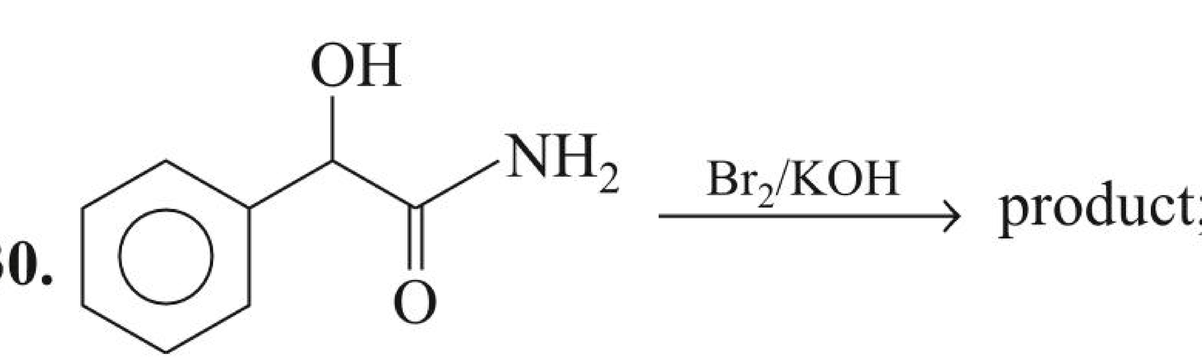


(1) 

(2) 

(3) 

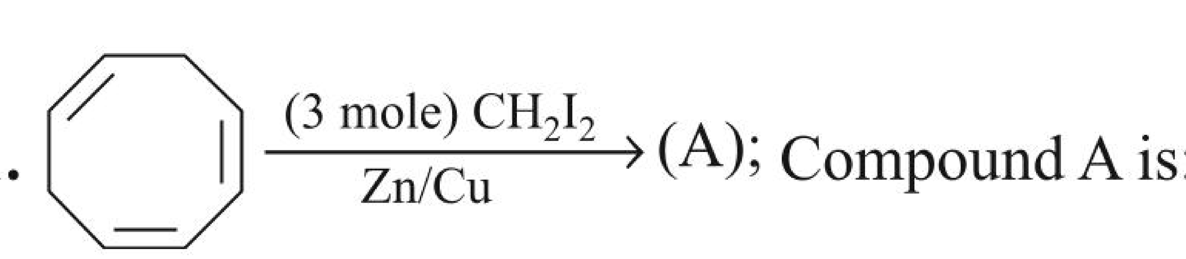
(4) all of these

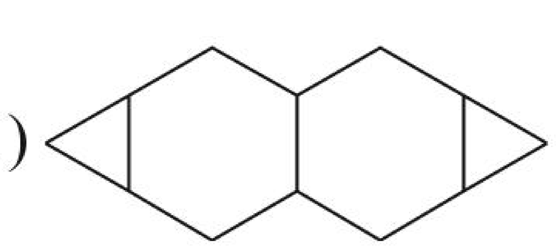
130. 

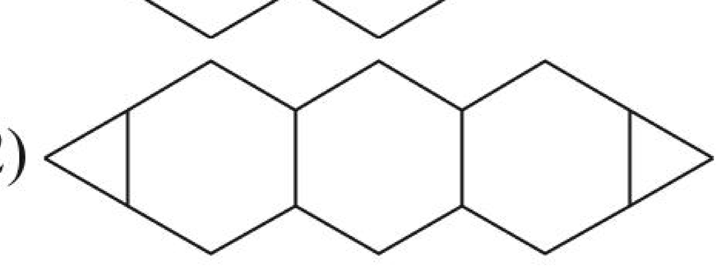
Product of this Hoffmann bromamide reaction is:

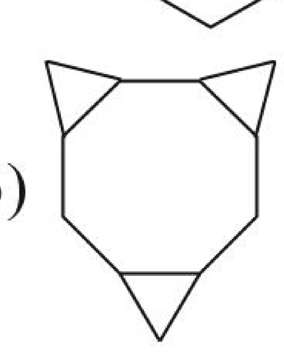
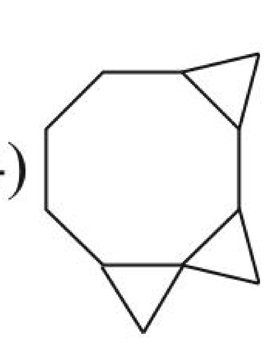
(1) $PhCH_2NH_2$ (2) PhCHO

(3) $PhCCH_3$ (with C=O) (4) $PhCH(OH)(NO_2)$

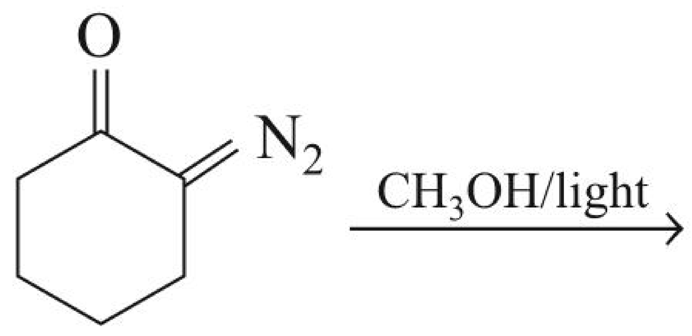
131. 

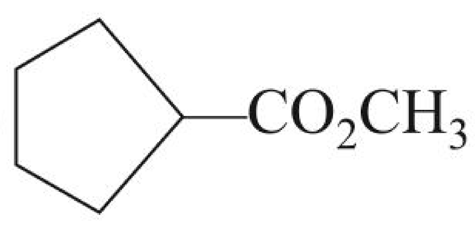
(1) 

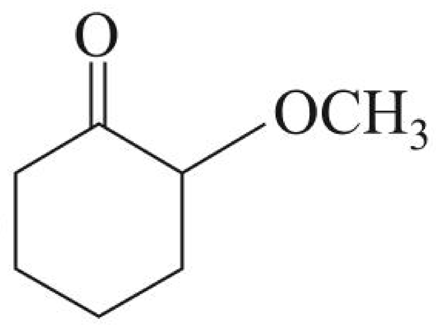
(2) 

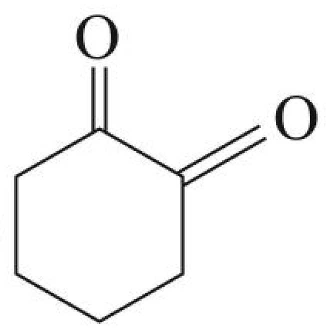
(3)  (4) 

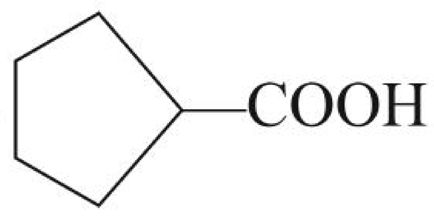
132. Identify the major product



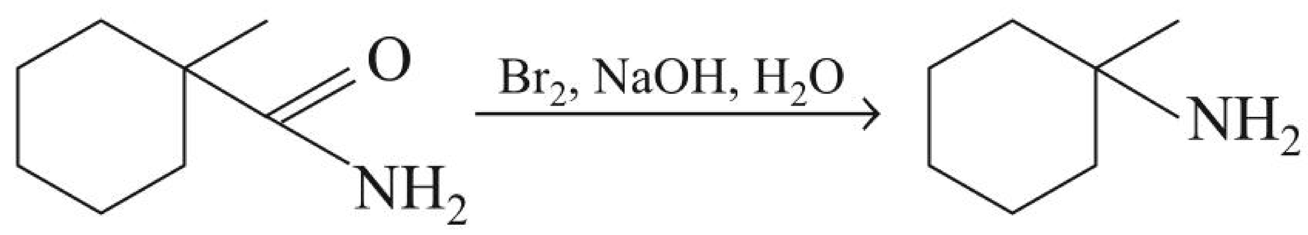
(1) 

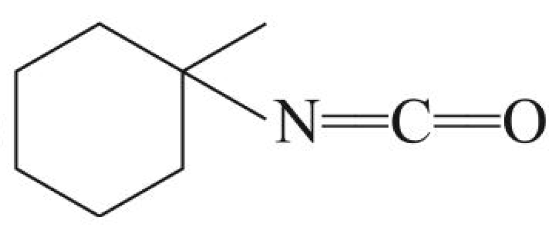
(2) 

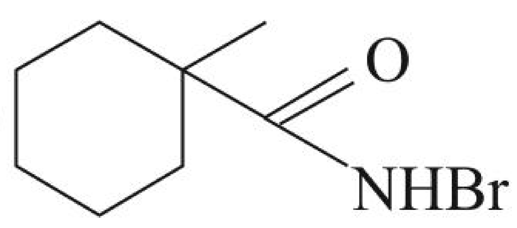
(3) 

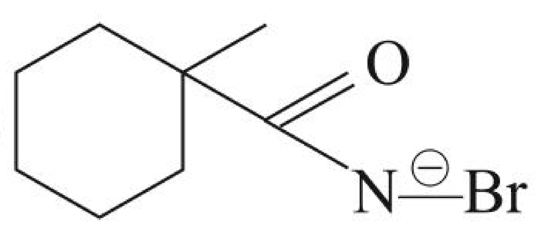
(4) 

133. Which of the following species would not be involved in the Hoffmann rearrangement shown below?



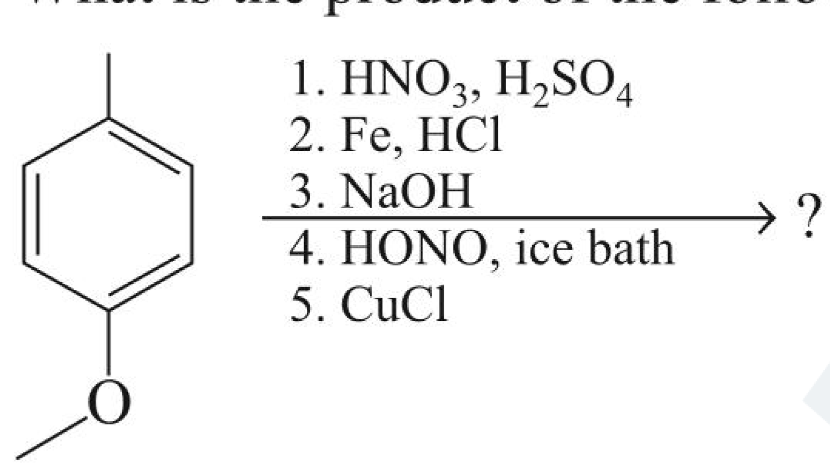
(1) 

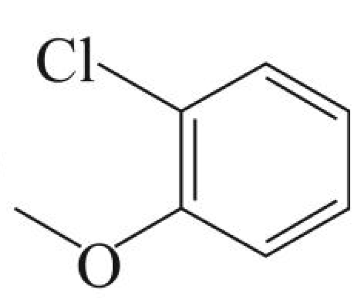
(2) 

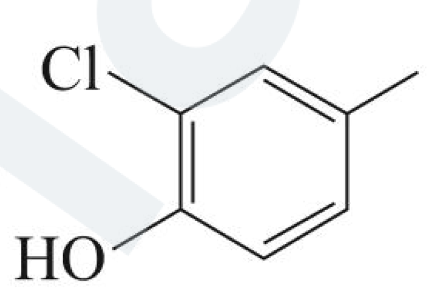
(3) 

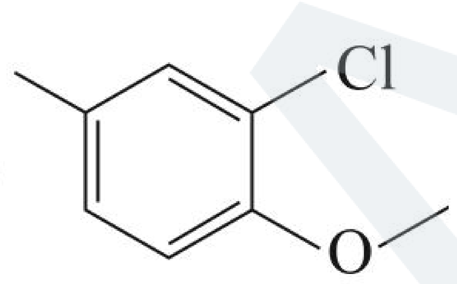
(4) All of the above are involved in the reaction.

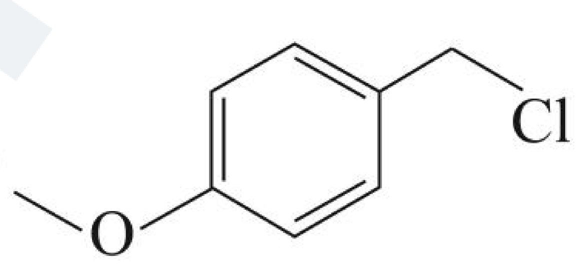
134. What is the product of the following synthesis?



(1) 

(2) 

(3) 

(4) 

135. $CH_3-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{KOBr} (A)$

$CH_3-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{LAH} (B)$

Relation between (A) and (B) is:

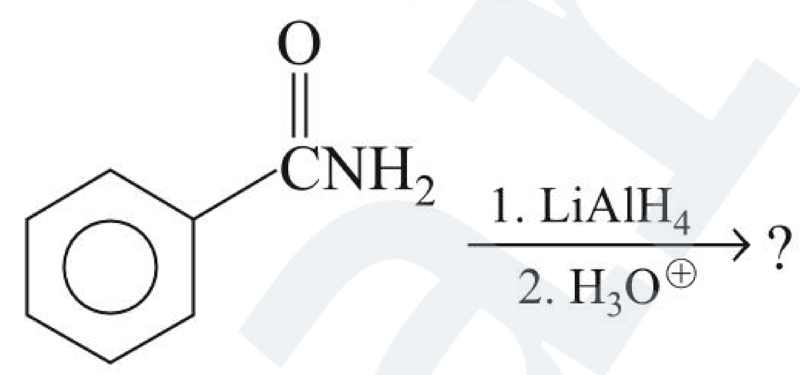
(1) Functional isomer (2) Homologues
(3) Chain isomer (4) Identical

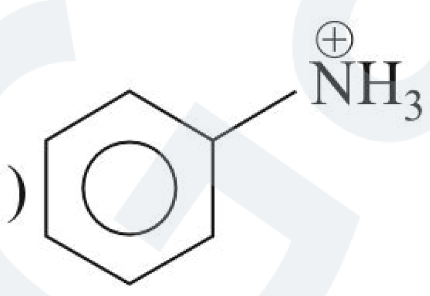
136. $Ph-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[P_2O_5/\Delta]{POCl_3} (A)$

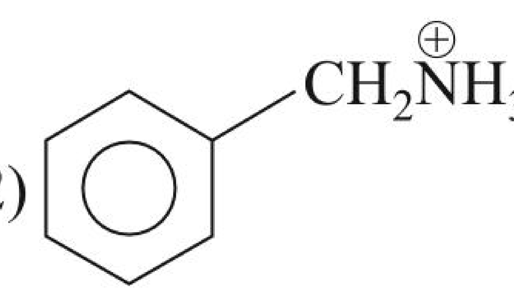
Product (A) is:

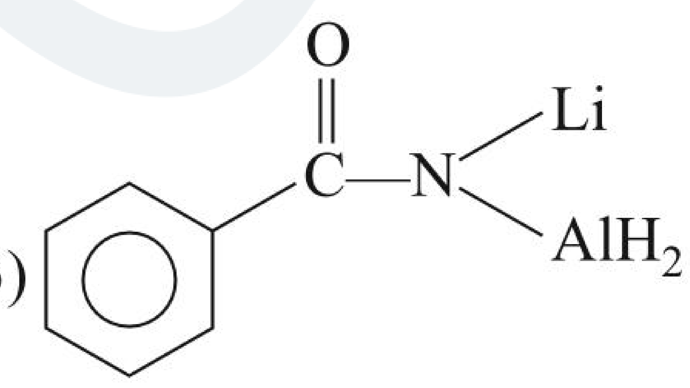
(1) $PhNH_2$ (2) $PhCH_2NH_2$
(3) $Ph-\overset{OH}{\overset{|}{C}H}-NH_2$ (4) $Ph-C\equiv N$

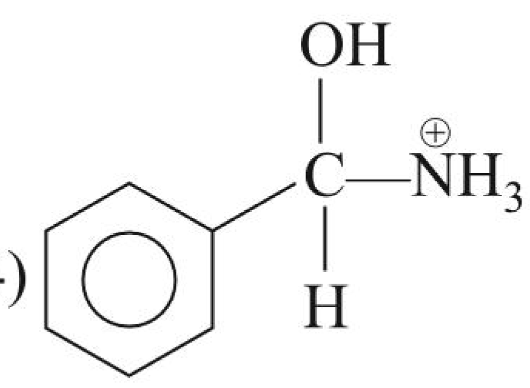
137. What is the major product of the following reaction?



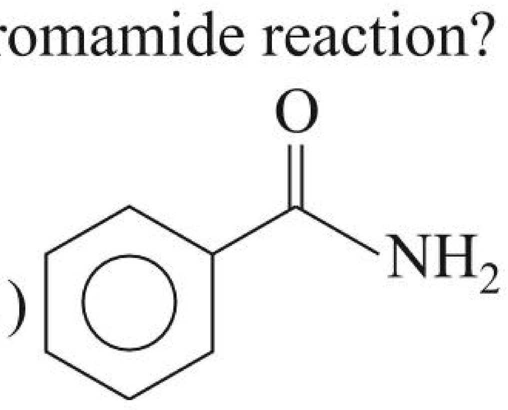
(1) 

(2) 

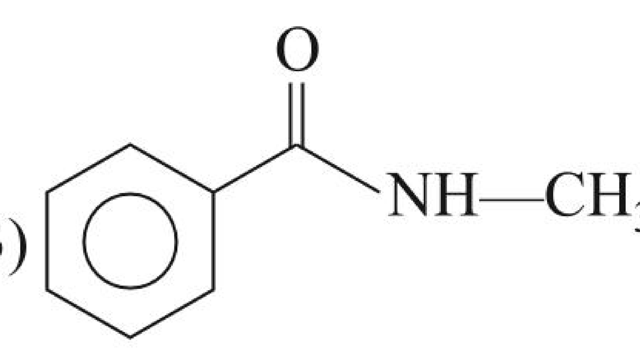
(3) 

(4) 

138. Which of the following will *not* undergo Hoffmann bromamide reaction?

(1) 

(2) $Ph-\overset{O}{\overset{\|}{C}}-NH-Br$

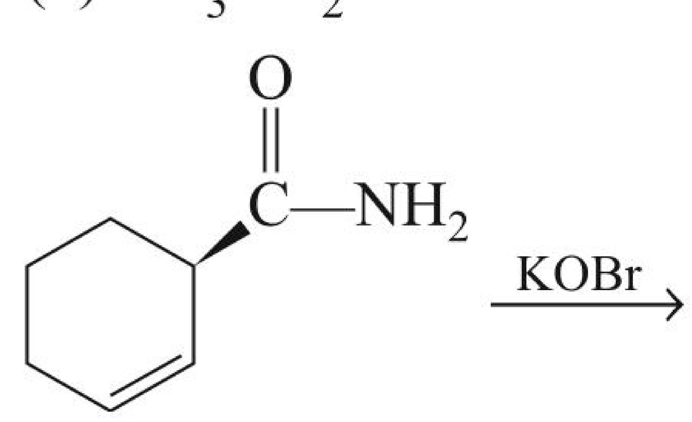
(3) 

(4) $CH_3-\overset{O}{\overset{\|}{C}}-NH_2$

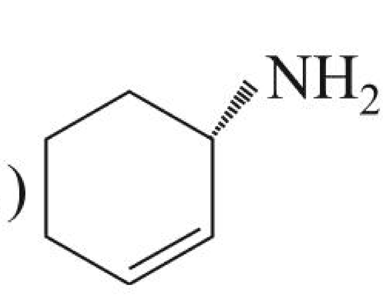
139. $CH_3-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[KOD/D_2O]{Br_2} (A)$

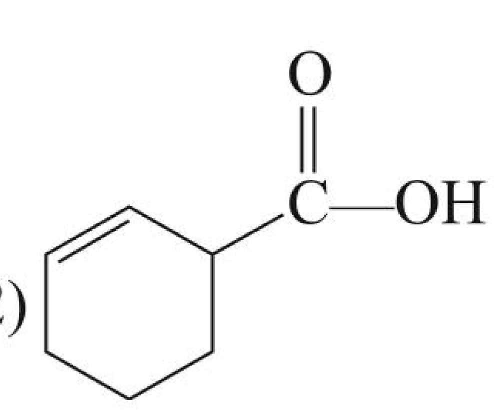
Product (A) is:

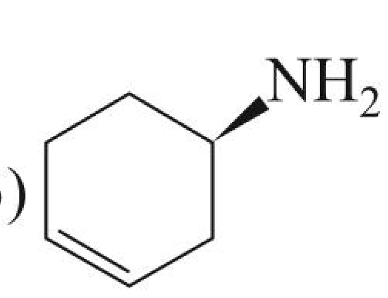
(1) CH_3OH (2) CH_3ND_2
(3) CH_3NH_2 (4) CH_3OD

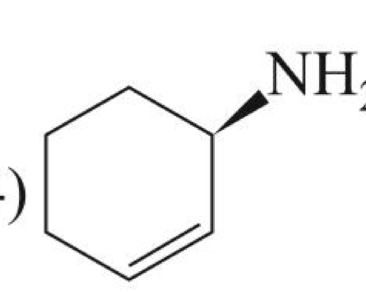
140. 

(A); Product A is:

(1) 

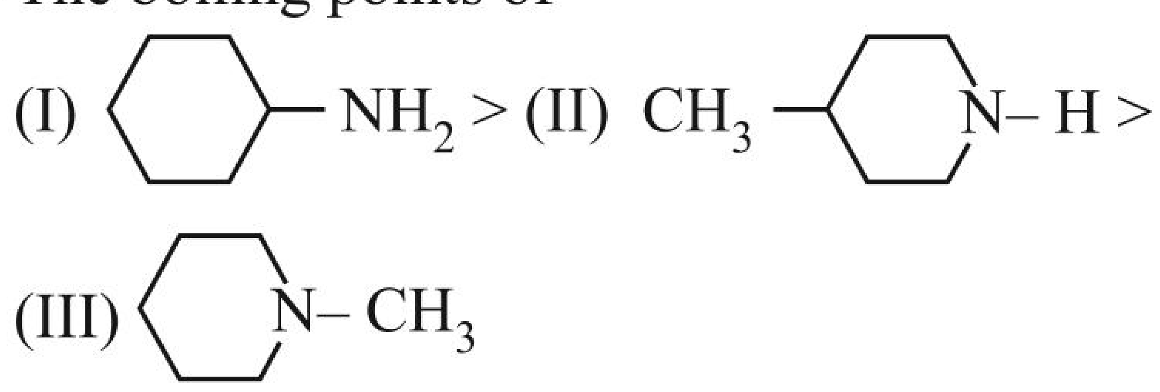
(2) 

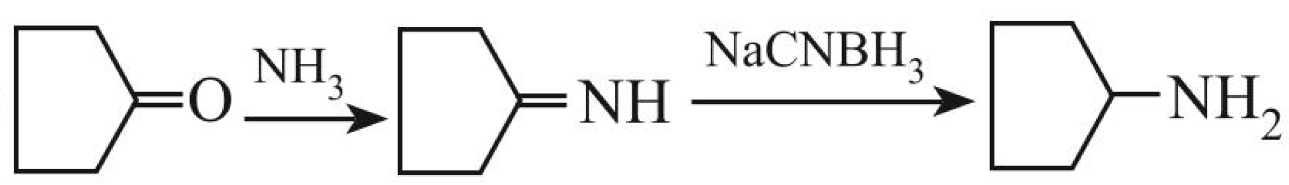
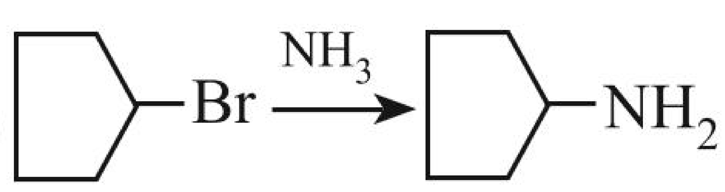
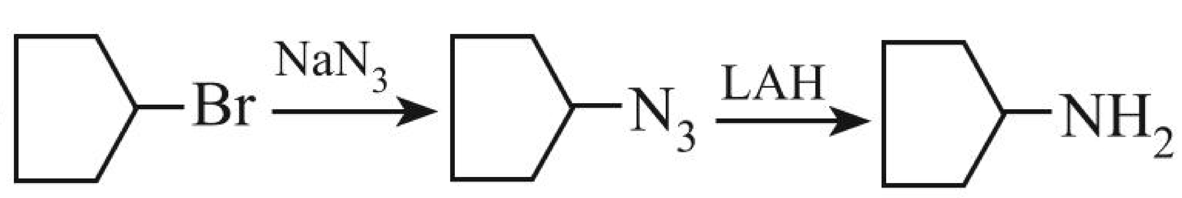
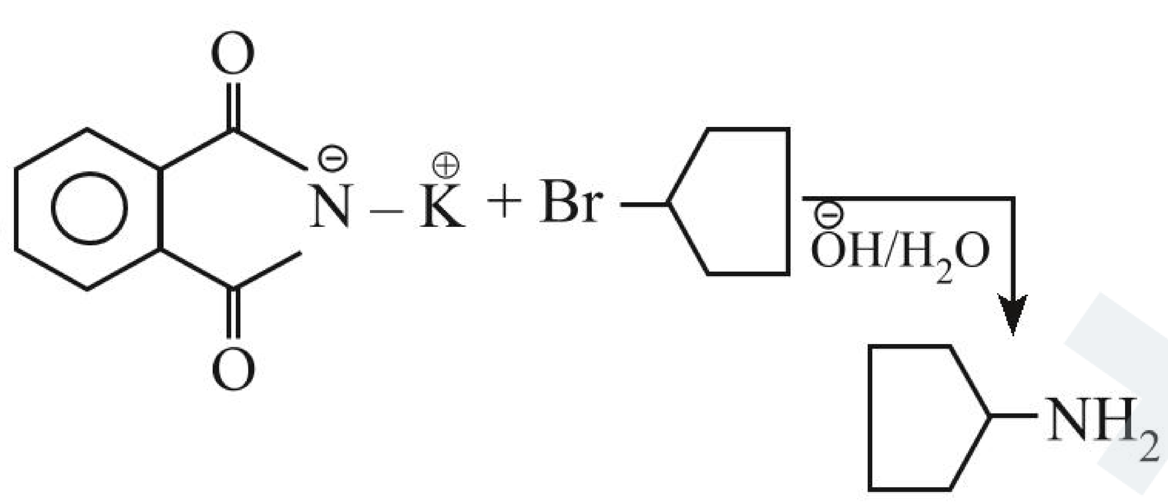
(3) 

(4) 

Multiple Correct Answers Type

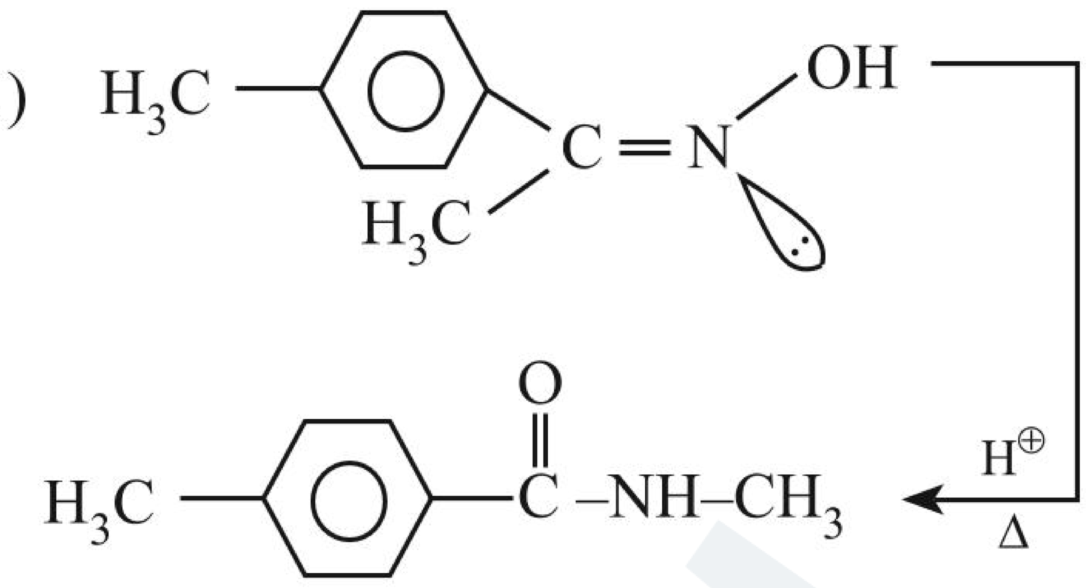
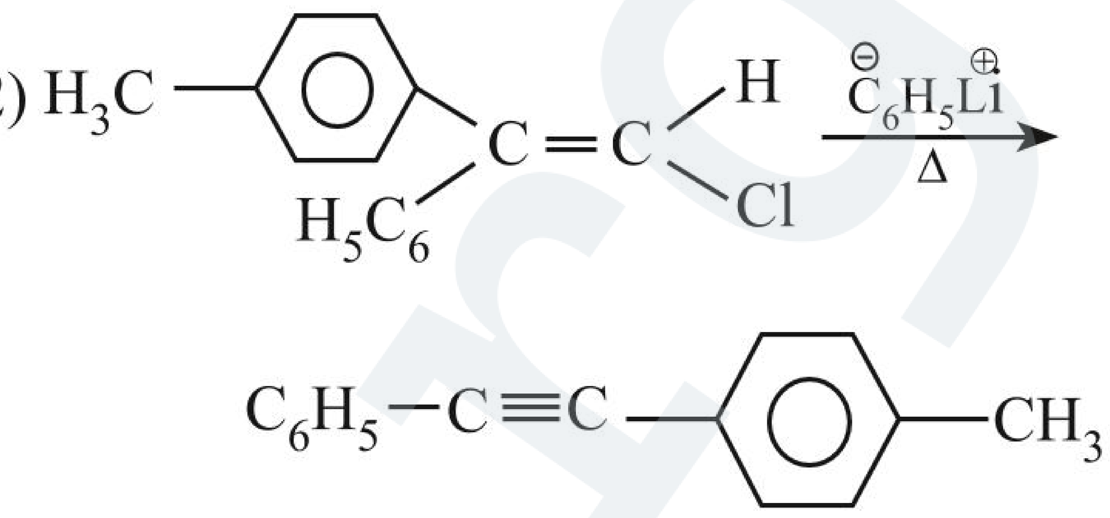
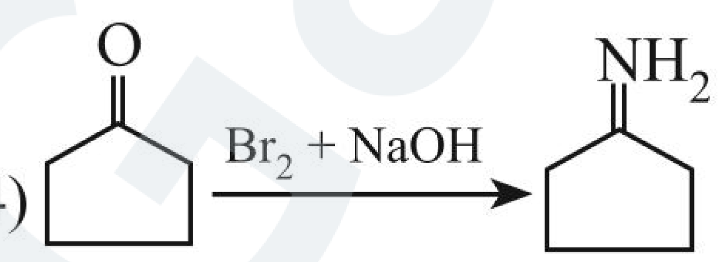
Preparation and Properties of Amines

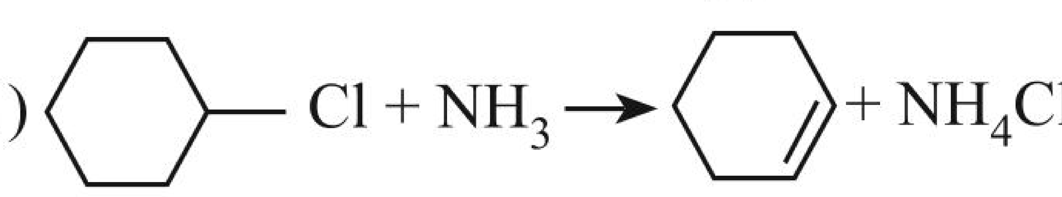
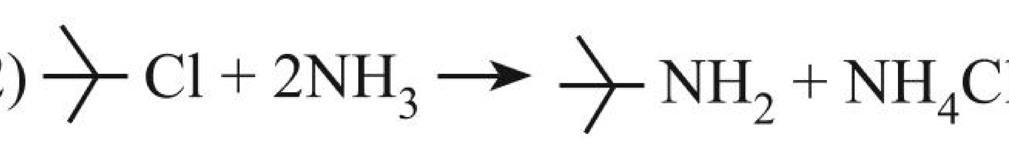
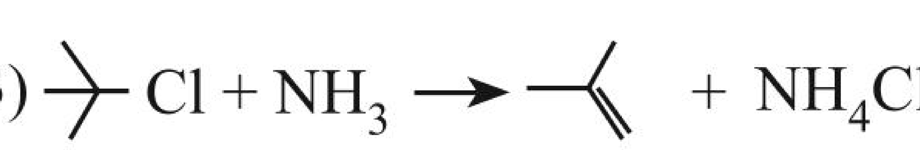
1. Which of the following statement are correct?
   (1) The extent of H-bonding is greater in 1° than 2° and 3° amines.
   (2) The boiling points of isomeric amines are in the order : 1° > 2° > 3°.
   (3) The boiling points of
   
   (4) The boiling points of
   (I) $C_4H_9NH_2$ > (II) $(CH_3)_2N—C_2H_5$ > (III) $(C_2H_5)_2NH$.

2. Which of the following are correct reactions?
   (1) 
   (2) 
   (3) 
   (4) 

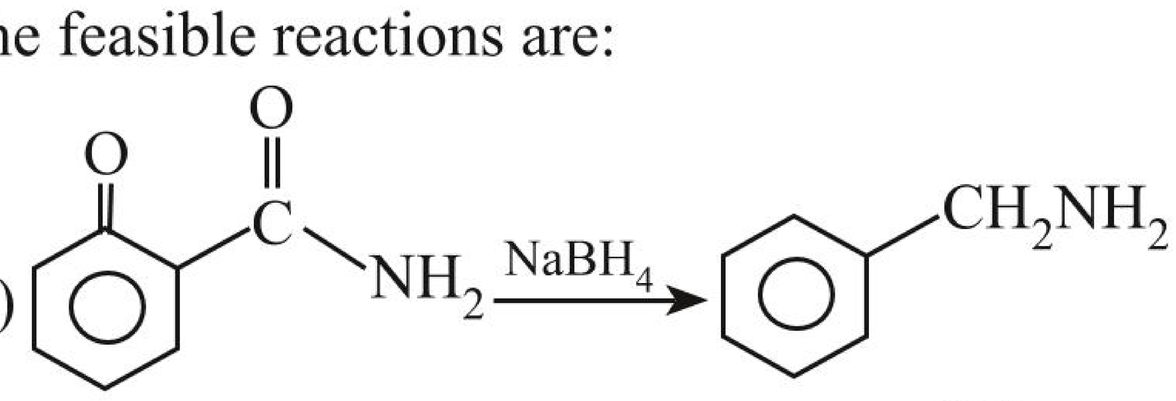
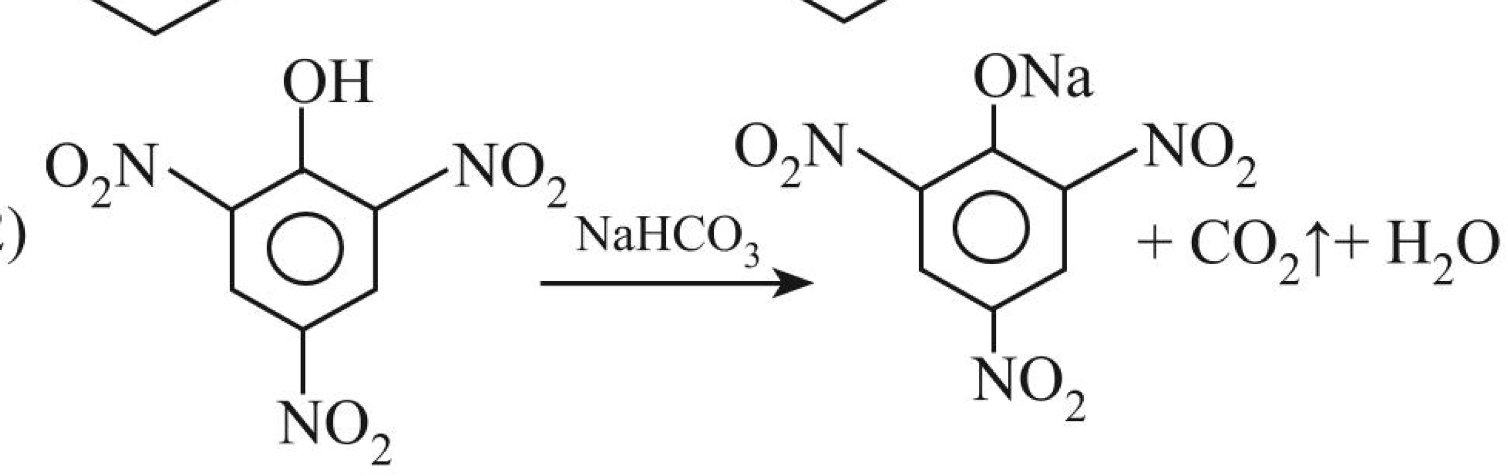
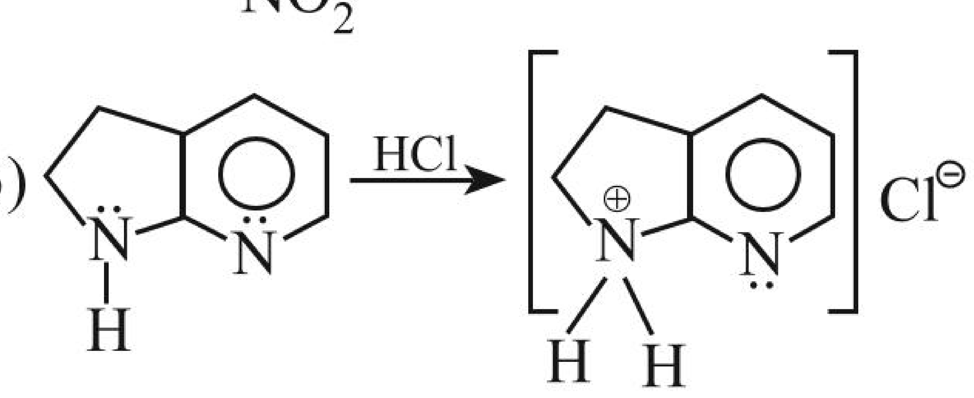
3. Which of the following statements are correct?
   (1) In gas phase, the basic character of amine is 3° > 2° > 1°. Due to the +I effect of (R–), the availability of lone pair electrons on N increases.
   (2) In aqueous medium, the basic character of amines is $(CH_3)_2NH > (CH_3)_3N > CH_3NH_2 > NH_3$.
   (3) In aqueous medium, the addition of protons increases crowding and thus strains setup, which being the highest in 3° amine decreases its basic character.
   (4) In aqueous medium, the ammonium ions in solution are stabilised not only by alkyl groups but also by H-bond donation to the solvent.

4. Guanidine, $(NH_2)_2\,C = NH$, is said to be the strongest nitrogen containing organic base because:
   (1) It has two —NH_2 groups.
   (2) It has three nitrogen atoms that can be protonated.
   (3) It is less stable as compared to the protonated species.
   (4) Its conjugate acid is very much stable due to three equivalent structure.

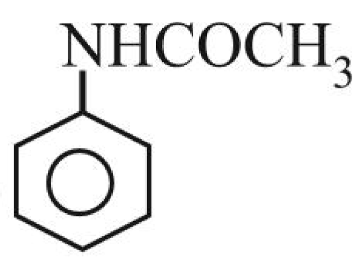
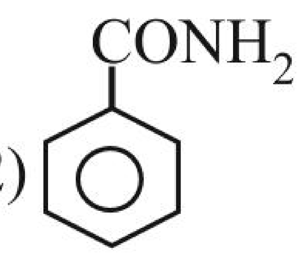
5. Which of the following reaction represent major products?
   (1) 
   (2) 
   (3) $C_6H_5-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{Br_2\,+\,KOH} C_6H_5-NH_2$
   (4) 

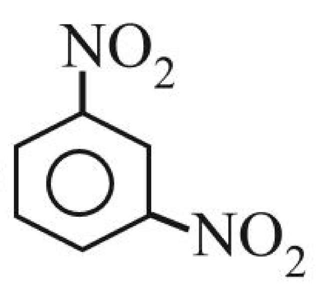
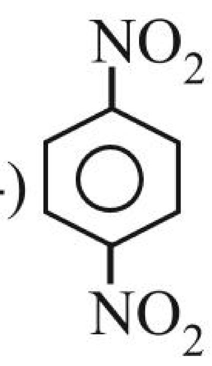
6. Which is/are correct reaction(s)?
   (1) 
   (2) 
   (3) 
   (4) 

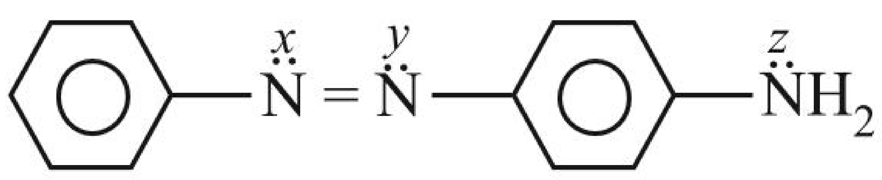
7. Butanonitrile may be prepared by heating:
   (1) Propyl alcohol with KCN
   (2) Propyl magnesium chloride with Cyanogen chloride
   (3) Butyl chloride with KCN
   (4) Propyl chloride with KCN

8. The feasible reactions are:
   (1) 
   (2) 
   (3) 
   (4) $CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-Br \xrightarrow{Na/ether} CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2 + CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-H$

9. A neutral benzenoid nitrogenous organic compound has zero dipole moment, its probable structure is:

(1)  (2) 

(3)  (4) 

10. 

The correct statement (s) about the compound P is/are:

(1) Nitrogen (x) is most basic in nature.
(2) The lone pair of electrons of nitrogen (z) is delocalized in the aromatic ring.
(3) All the nitrogen x,y and z are sp^2 hybridized.
(4) The compound P has stereoisomers.

11. When a nitrogenous substance X is treated with nitrous acid, a blue colour is obtained. The compound X can be:

(1) $CH_3CH_2NO_2$ (2) $(CH_3)_2CHNO_2$
(3) CH_3CH_2ONO (4) $(CH_3CH)_2ONO$

12. Which of the following can exist as inner salt?

(1) *p*-Aminobenzenesulphonic acid
(2) *p*-Aminobenzoic acid
(3) Aminoacetic acid
(4) Alanine

13. Which of the following reactions can be used for preparing aniline?

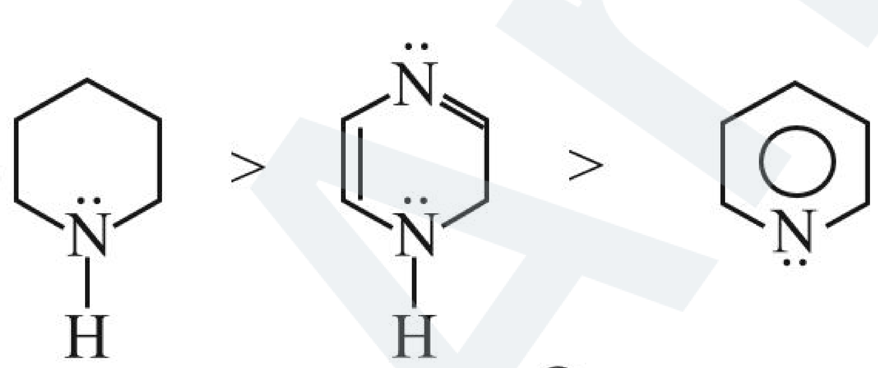
(1) $C_6H_5COOH \xrightarrow{N_3H,\ conc.\ H_2SO_4}$

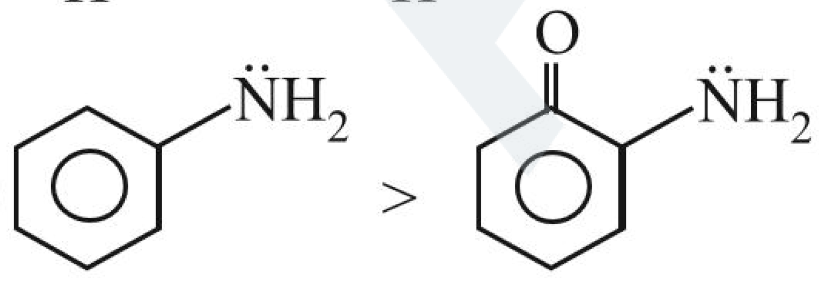
(2) $C_6H_5NC \xrightarrow{H_3O^{\oplus}}$

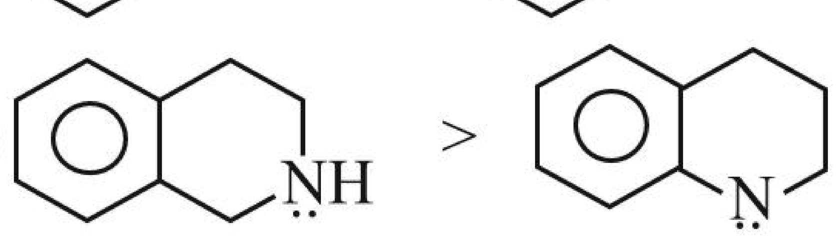
(3) $C_6H_5NC \xrightarrow{LiAlH_4}$

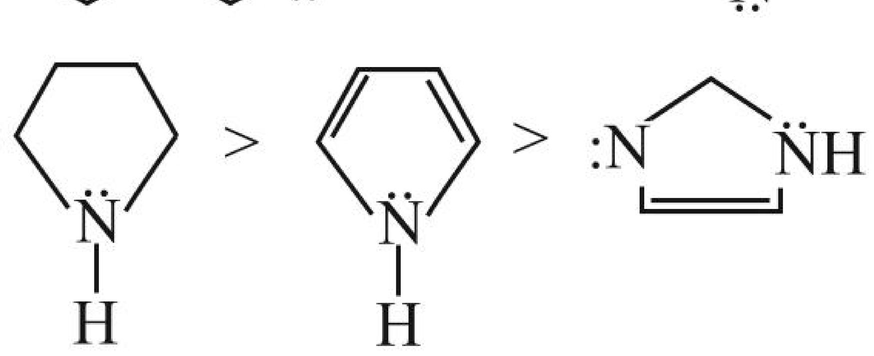
(4) $C_6H_5CONH_2 \xrightarrow{Br_2/NaOH}$

14. Which of the following are the correct orders of basic character?

(1) 

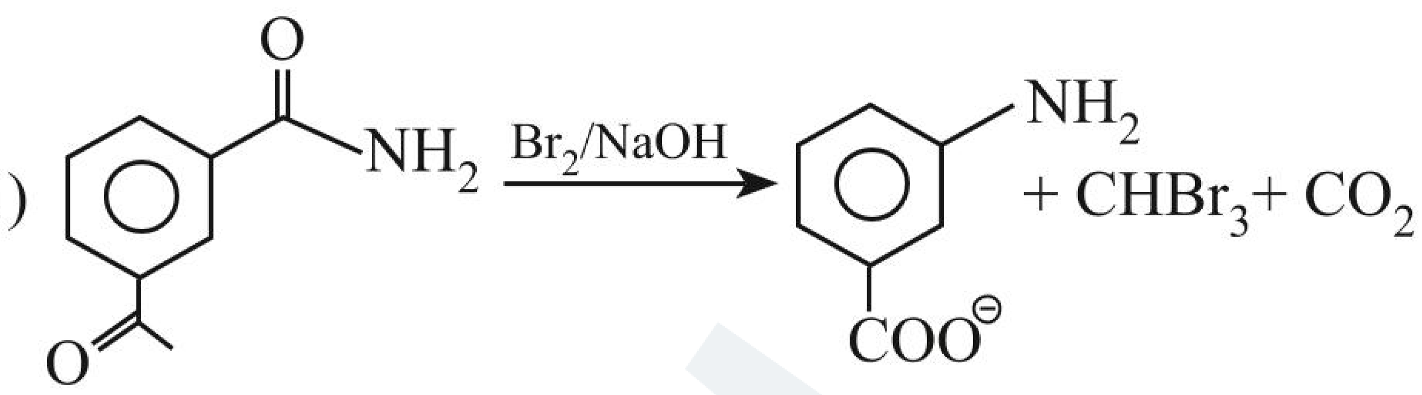
(2) 

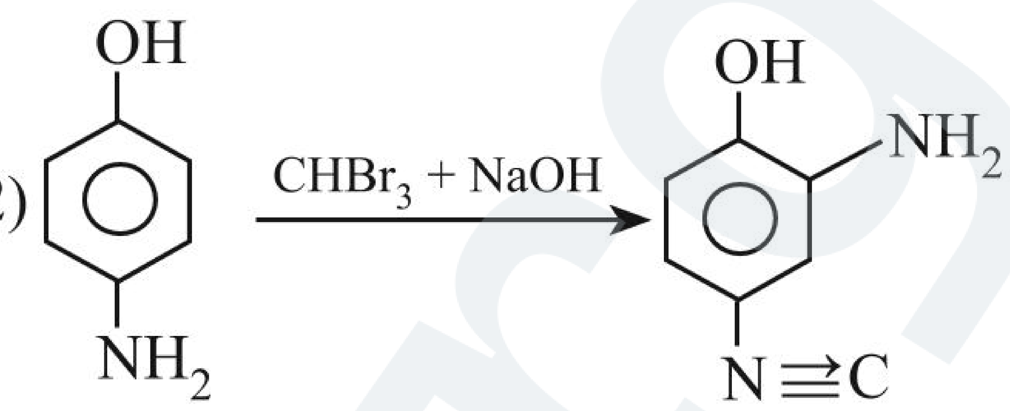
(3) 

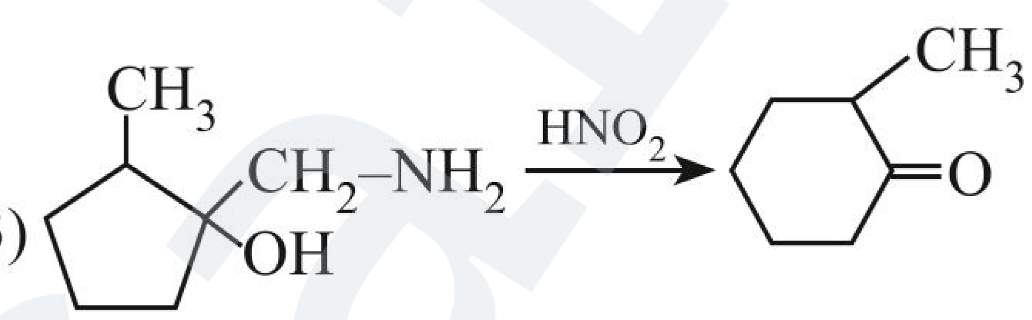
(4) 

Diazotisation and Rearrangement

15. In which reaction, major product formed is correct?

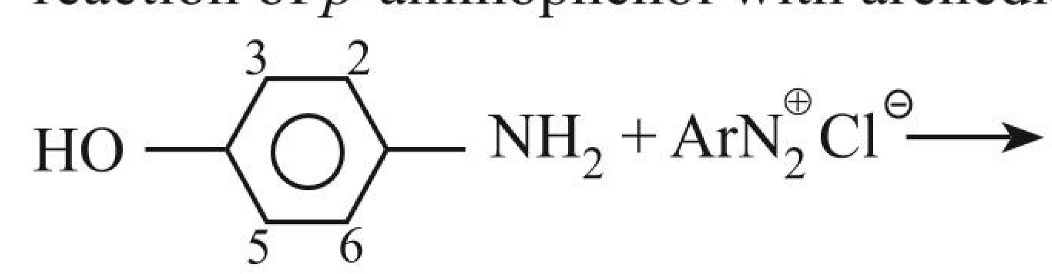
(1) 

(2) 

(3) 

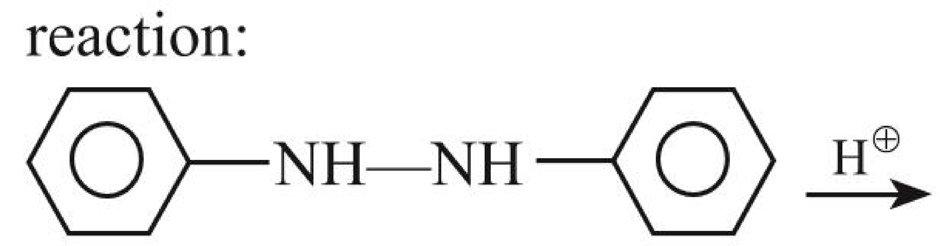
(4) $R\text{–}\underset{\underset{O}{\|}}{C}\text{–}NH_2 \xrightarrow{HNO_2} R\text{–}\underset{\underset{O}{\|}}{C}\text{–}OH$

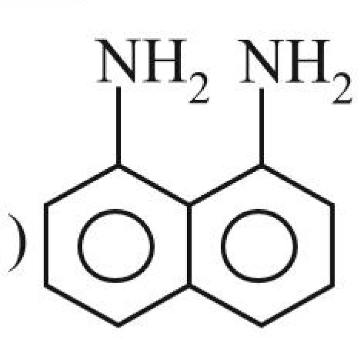
16. Which of the following statements is ture regarding the reaction of *p*-aminophenol with arenediazonium chloride?

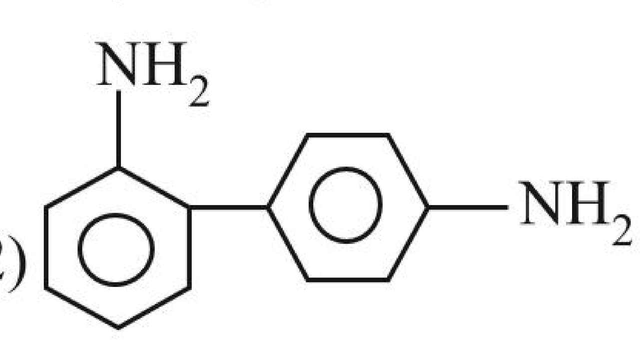


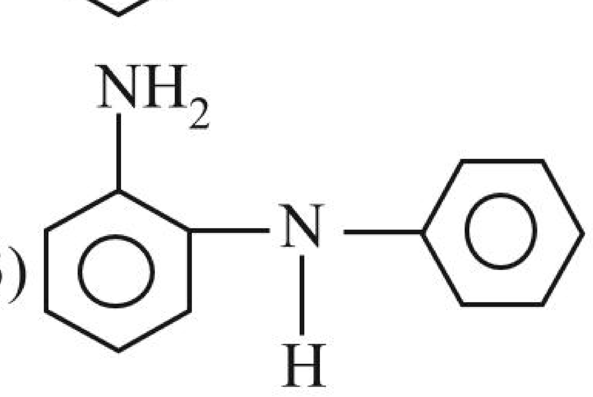
(1) Reaction takes place at position 2 in presence of HCl.
(2) Reaction takes place at position 3 in presence of NaOH.
(3) No reaction occurs.
(4) Four azo groups can be introduced in the molecule.

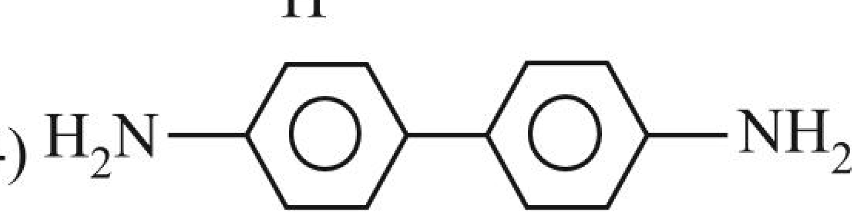
17. Find out products which are formed by the following reaction:



(1) 

(2) 

(3) 

(4) 

18. The presence of primary amine can be confirmed by its reaction with:

(1) H_2SO_4 (2) $CHCl_3 + NaOH$
(3) CS_2 and $HgCl_2$ (4) HNO_2

19. Which are related with Curtius rearrangement?

(1) $R—\overset{\overset{O}{\|}}{C}—OH$ (2) $R—NH_2$

(3) $R—\overset{\overset{O}{\|}}{C}—Cl$ (4) NaN_3

20. Which of the following reaction can be used to make ethyl isocyanide?

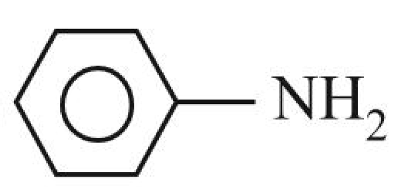
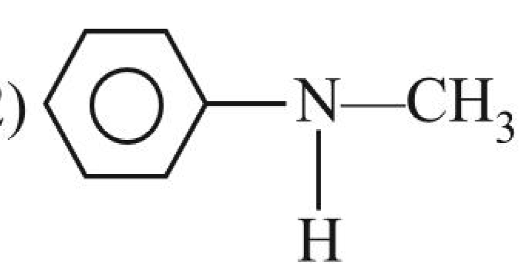
(1) $CH_3CH_2Br + KCN \longrightarrow$

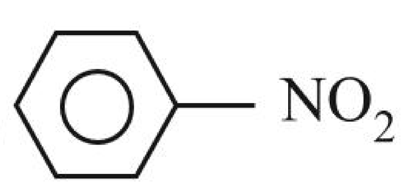
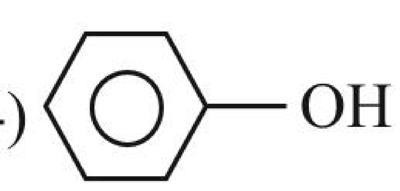
(2) $CH_3CH_2Br + AgCN \longrightarrow$

(3) $CH_3CH_2—NH—\underset{\underset{O}{\|}}{C}—H \xrightarrow{POCl_3}$

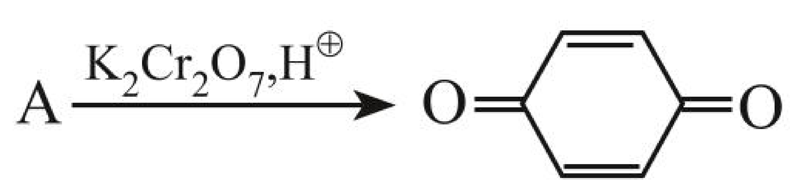
(4) $CH_3CH_2NH_2 + CHCl_3 \xrightarrow[\Delta]{KOH}$

21. Which of the following given Liebermann nitroso reaction?

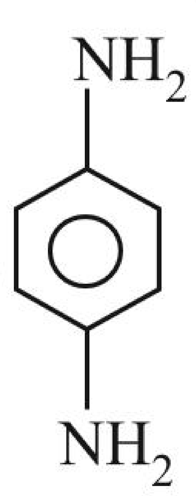
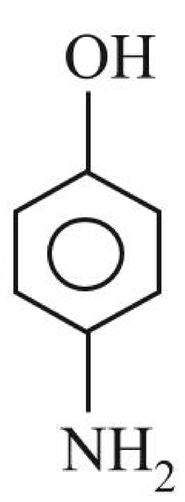
(1)  (2) 

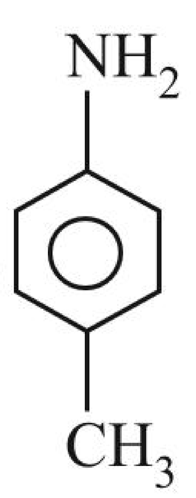
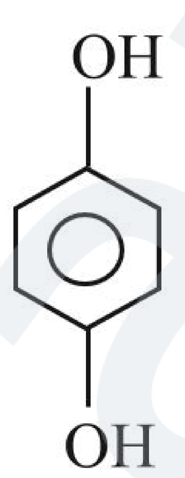
(3)  (4) 

22 Consider the following reaction:



The starting substance A can be:

(1)  (2) 

(3)  (4) 

23. Reaction involves isocyanate as intermediate product:

(1) Hoffmann rearrangement

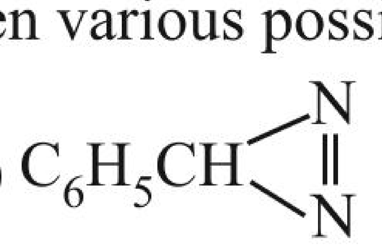
(2) Lossen rearrangement

(3) Schmidt rearrangement

(4) Curtius rearrangement

24. $C_6H_5—CH_2—I \xrightarrow[\Delta]{NaN_3}$ Products :

Reaction is assumed to involve nitrene as intermediate, then various possible products are:

(1)  (2) $C_6H_5N=CH_2$

(3) $C_6H_5CH=NH$ (4) $C_6H_5CH_2NH_2$

25. By which of the following reaction can methylcyanide be prepared?

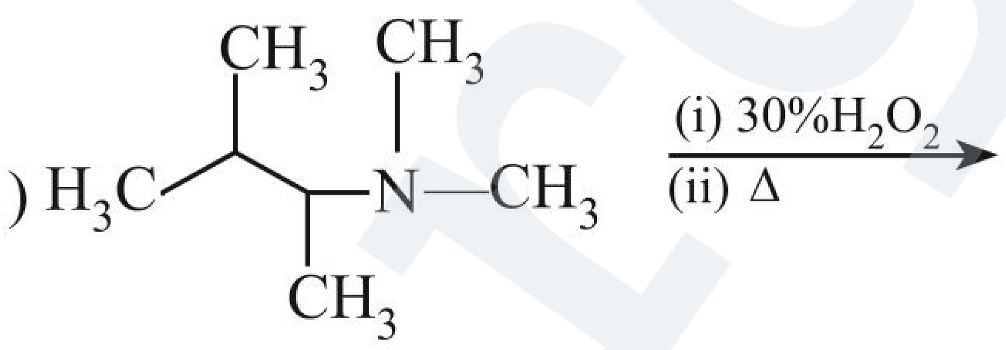
(1) $CH_3—\overset{\overset{O}{\|}}{C}—NH_2 \xrightarrow[\Delta]{P_4O_{10}}$

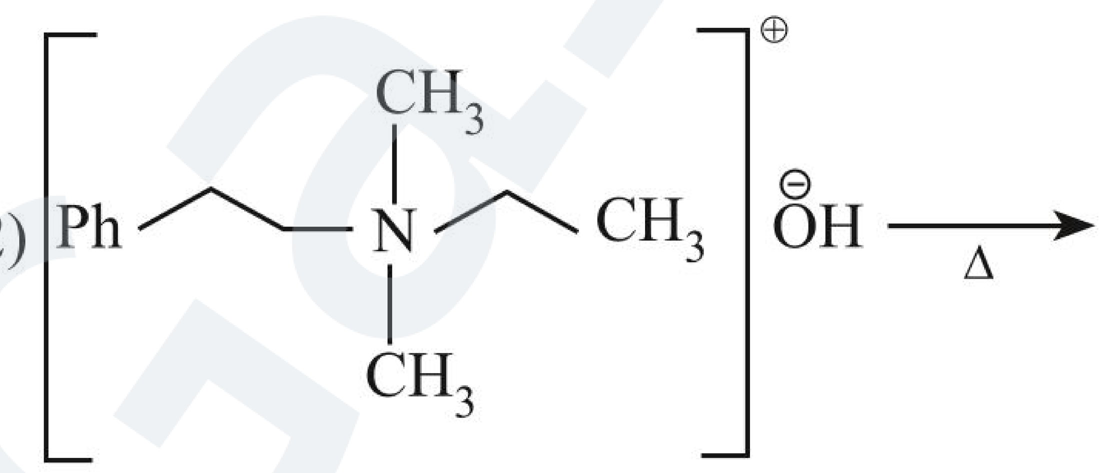
(2) $CH_3NH_2 + CHCl_3 \xrightarrow{KOH}$

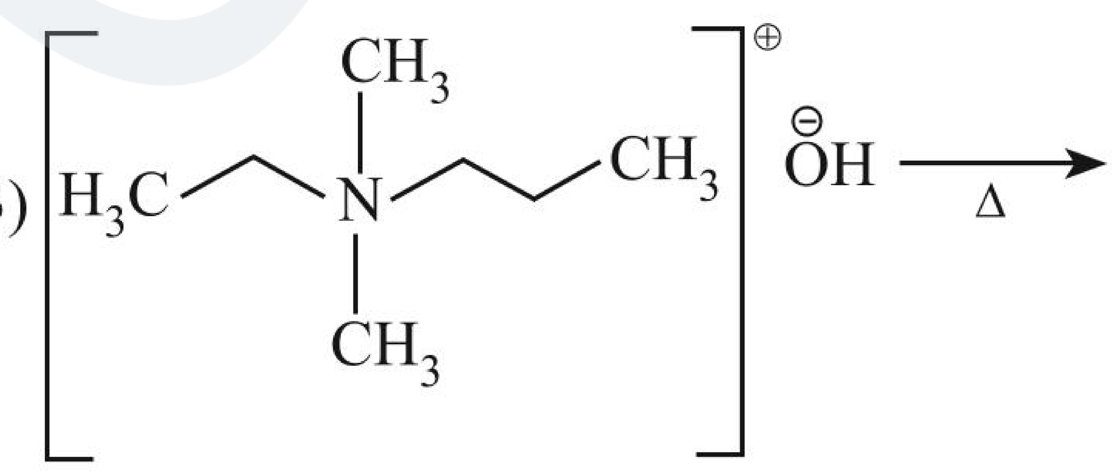
(3) $CH_3—CH=N—OH \xrightarrow[\Delta]{P_2O_5}$

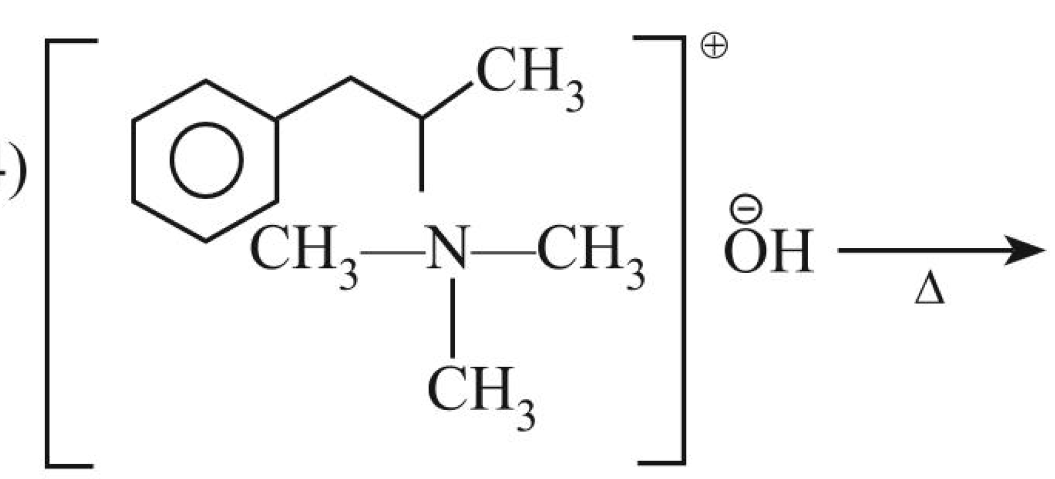
(4) $CH_3Br \xrightarrow[DMF]{KCN}$

26. Which of the following would give Hoffmann alkene?

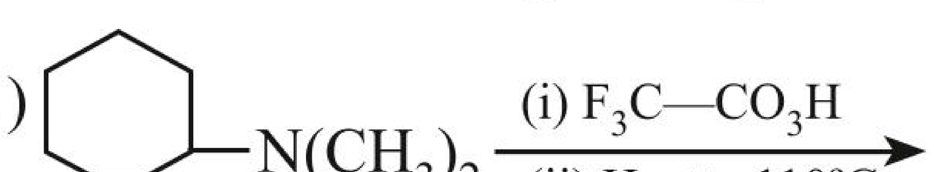
(1) 

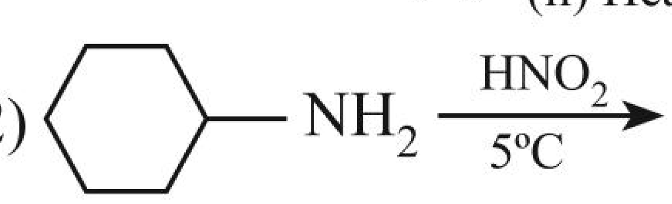
(2) 

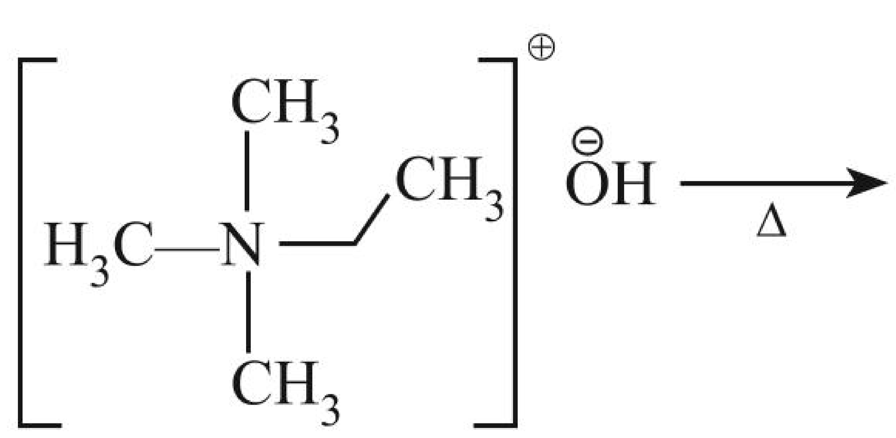
(3) 

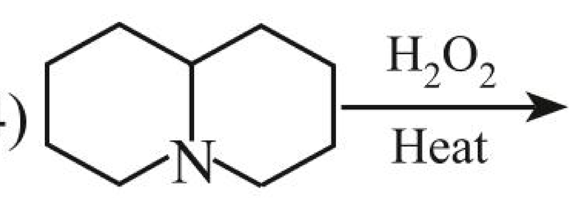
(4) 

27. Which of the following are Cope reactions?

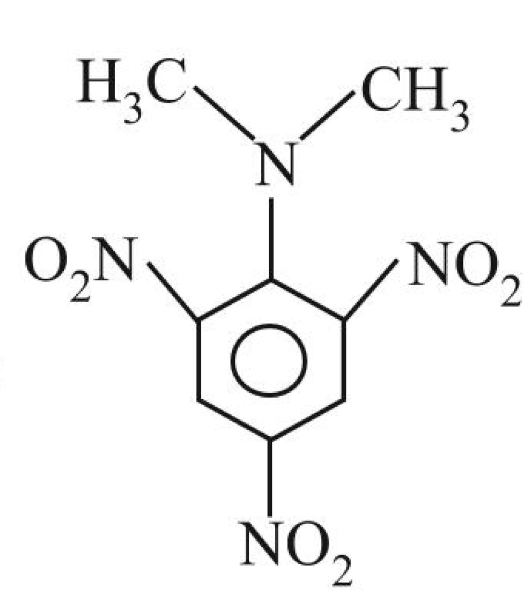
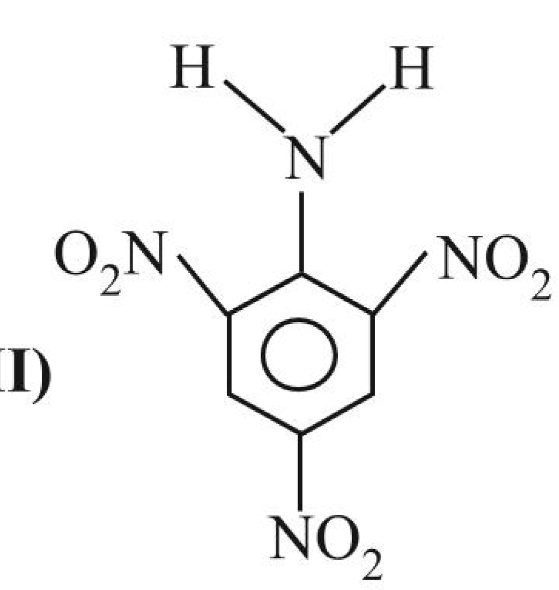
(1) 

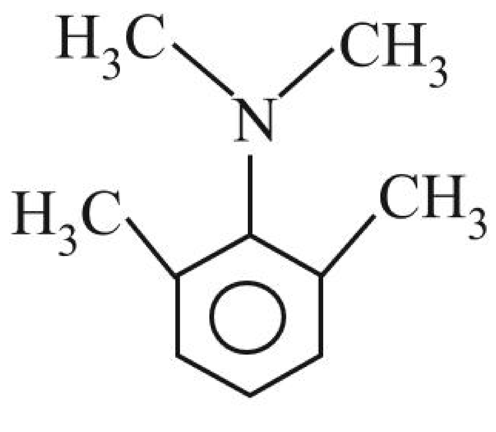
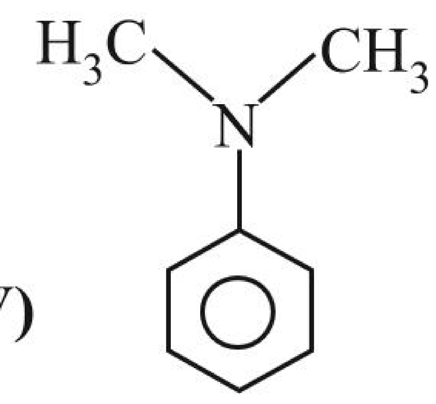
(2) 

(3) 

(4) 

28. Consider the structures :

(I)  **(II)** 

(III)  **(IV)** 

Which of the following statements are correct?

(1) Basic strength of I is less than that of II

(2) Basic strength of I is greater than II

(3) Basic strength of III is less than that of IV

(4) Basic strength of III is greater than IV

29. Which of the following statements are correct?

(1) Aryldiazonium ions are more stable than alkyldiazonium ions.

(2) Electron release from the *ortho*-and *para*-positions of the ring stabilises the aryldiazonium ion.

(3) The increased stability of aryldiazonium is due to the great diffculty of forming $Ar^{\oplus}$ as compared to $R^{\oplus}$.

(4) Alkyldiazonium is more stable than aryldiazonium ion.

Cyanides, Isocyanides and Nitro Compounds

30. Which of the following statements are correct?

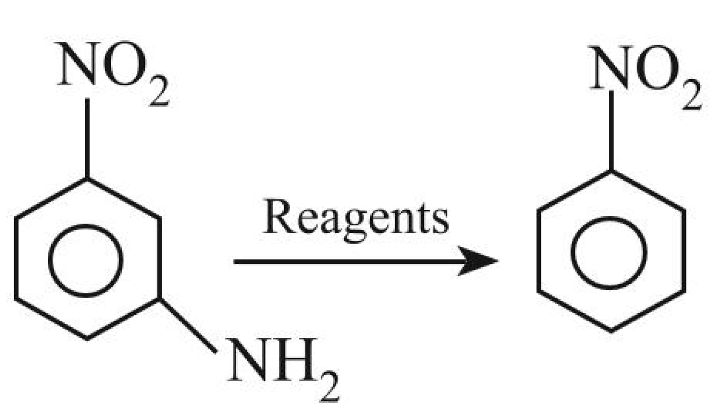
(1) Isocyanides are hydrolysed with dilute acids and not by alkali.

(2) Cyanides are hydrolysed with aqueous mineral acids or alkali.

(3) Ethanenitrile on complete hydrolysis gives acetic acid and NH_3.

(4) Ethanenitrile on partial hydrolysis gives acetamide.

31. Which of the following reagents are correct for the given reaction?



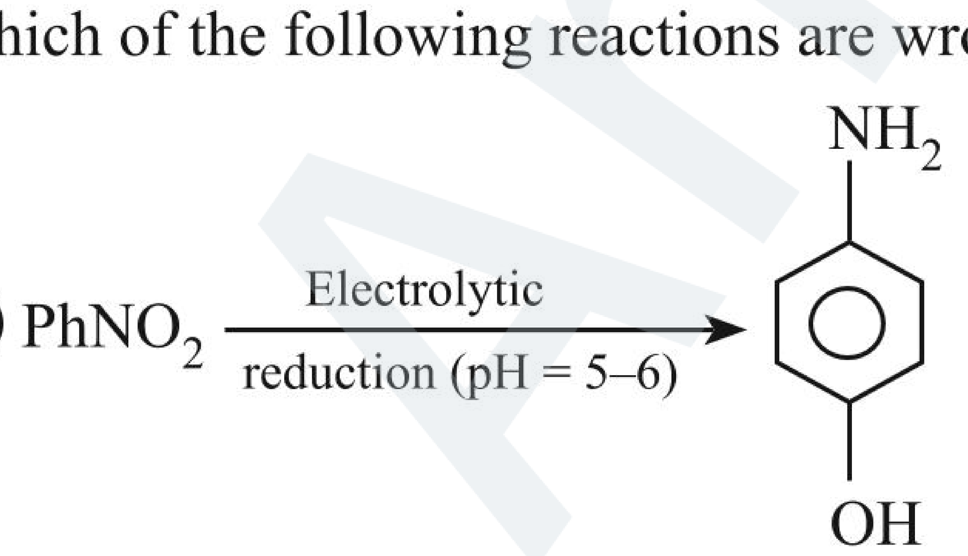
(1) i. HNO_2 ii. C_2H_5OH and heat

(2) i. KNO_2 + HBr, 0–5ºC ii. Na_2SnO_2

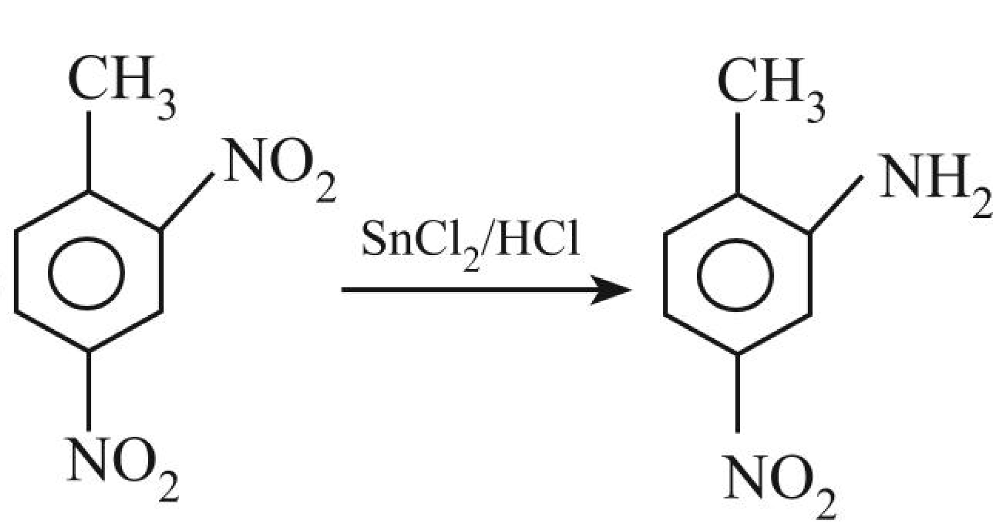
(3) i. $NaNO_2$ + HCl, 0–5ºC ii. H_3PO_2

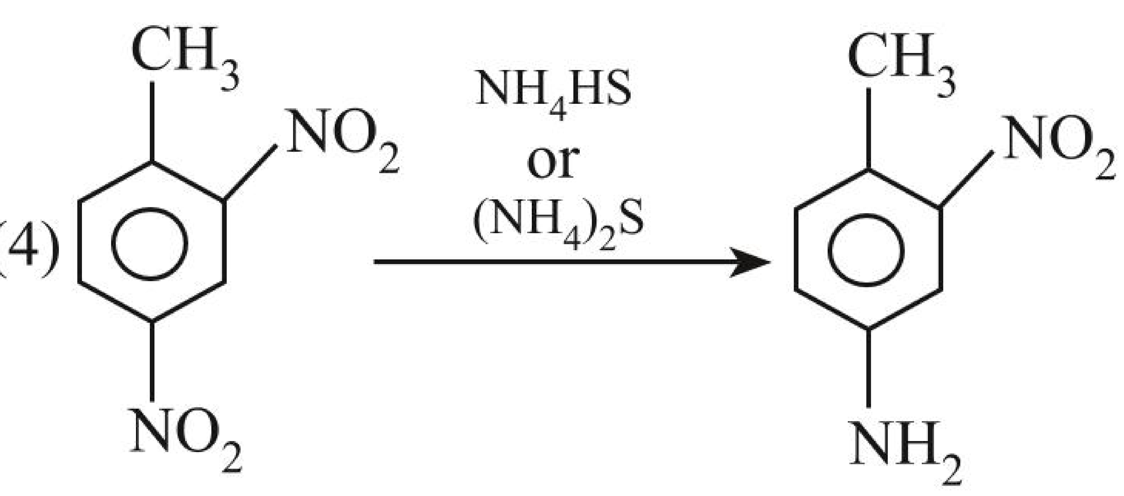
(4) i. KNO_2 + HCl ii. H_2O (steam)

32. Which of the following reactions are wrong?

(1) 

(2) $PhNO_2 \xrightarrow[\text{reduction (pH = 3–4)}]{\text{Electrolytic}} PhNHOH$

(3) 

(4) 

33. By which of the following reaction can MIC (methylisocyanate) be obtained?

(1) $CH_3—\overset{\oplus}{N}\equiv\overset{\ominus}{C}$ + DMSO ⟶

(2) $CH_3—\overset{\oplus}{N}\equiv\overset{\ominus}{C} + O_3$ ⟶

(3) $CH_3—\overset{\oplus}{N}\equiv\overset{\ominus}{C}$ + S ⟶

(4) $CH_3—\overset{\oplus}{N}\equiv\overset{\ominus}{C}$ + HgO ⟶

34. Which of the following statement are correct?

(1) 3º nitro compound does not react with HNO_2.

(2) 2º nitro compound with HNO_2 gives pseudo nitrole, which gives blue colour with base.

(3) 1º nitro compound with HNO_2 gives nitrolic acid, which gives blood-red colour with base.

(4) 1º ,2º , and 3º nitro compounds can be distinguished by HNO_2.

35. Which statements are correct about MIC (methyl isocyanate, CH_3–N=C=O)

(1) MIC is prepared by the reaction of CH_3NH_2 and $COCl_2$ (phosgene)?

(2) Hydrolysis of MIC gives $\left(CH_3—NH—\overset{\overset{\large O}{||}}{C}—OH\right)$ as the intermediate, which gives CH_3NH_2 and CO_2 on further hydrolysis.

(3) MIC is used to prepare insecticide, carbaryl under the commercial name Sevin.

(4) (N=C) bond takes part when 1-naphthol is reacted with MIC because N is more basic and nuclephilic.

36. Which of the following statement are correct?

(1) In an isocyanide, first an electrophile and then a nucleophile add at the same C atom bearing negative charge.

(2) $CH_3\overset{\oplus}{N}\equiv\overset{\ominus}{C}$ on complete hydrolysis gives CH_3NH_2 and HCOOH.

(3) $CH_3\overset{\oplus}{N}\equiv\overset{\ominus}{C}$ on partial hydrolysis gives N-methyl methanamide.

(4) In an isocyanide, first a nucleophile and then an electrophile add at the same C atom bearing negative charge.

37. Which of the following reactions is/are correct?

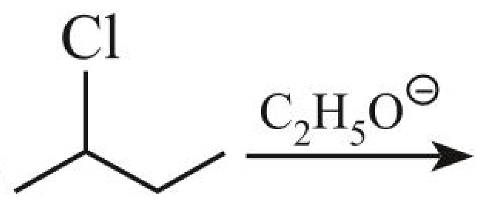
(1) $PhNO_2 \xrightarrow{Al—Hg/H_2O} Ph—NH—NH—Ph$

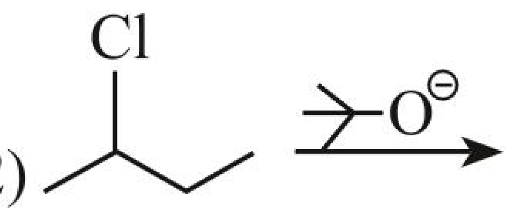
(2) $PhNO_2 \xrightarrow[+\ NaOH]{Na_2SnO_2} Ph—N{=}N—Ph$

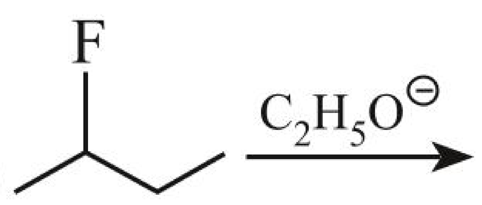
(3) $PhNO_2 \xrightarrow{Na_3AsO_3 + NaOH} Ph-\overset{\oplus}{N}(O^{\ominus})=N-Ph$

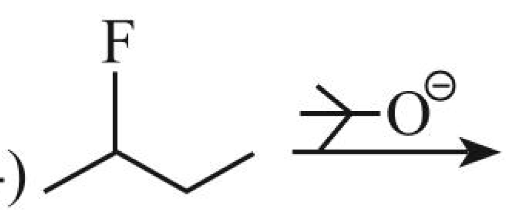
(4) $PhNO_2 \xrightarrow{LAH} PhNH_2$

38. Which of the following would give Hoffmann alkene?

(1) 

(2) 

(3) 

(4) 

39. Which statement are correct?

(1) Aniline couples with diazonium salt in mild acidic condition (pH = 4–6)

(2) Phenol couples with diazonium salt in mild basic conditions (pH = 8–10)

(3) Phenol and aniline give coupling reaction with diazonium salt.

(4) Both phenol and aniline couple with diazonium slat in neutral condition (pH =7).

40. Which of the following statement are correct?

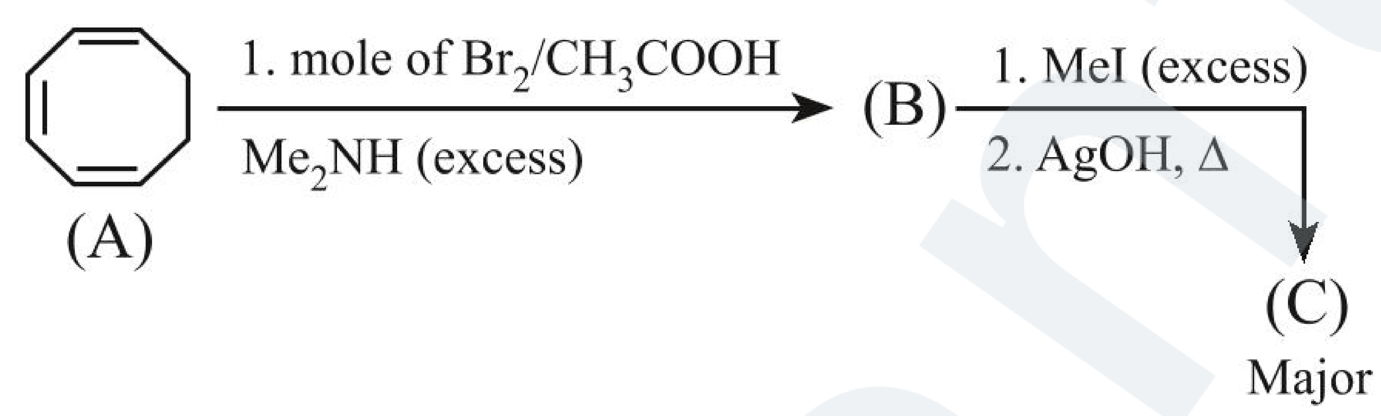
(1) δ-Amino acids on heating give lactam (six-membered cyclic ester).

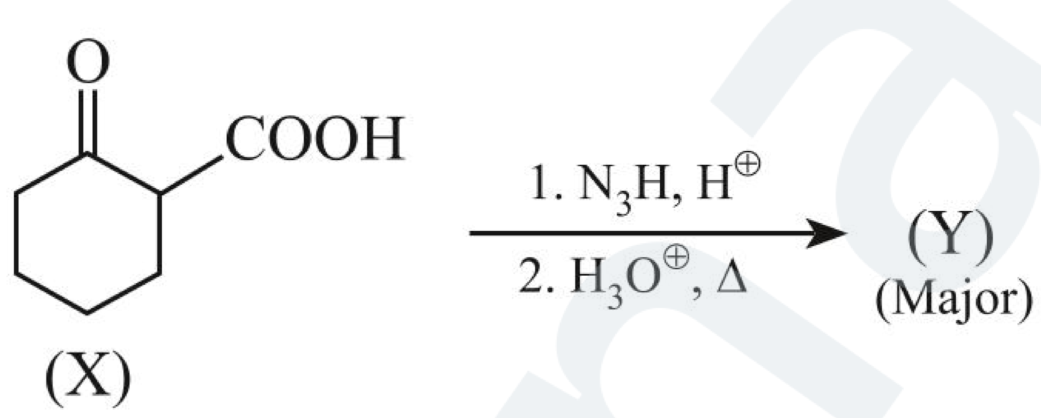
(2) γ-Amino acids on heating give lactam (five-membered cyclic ester).

(3) β-Amino acids on heating give α,β-unsaturated acids.

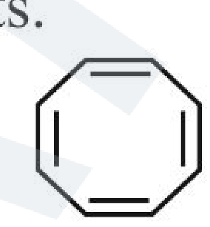
(4) α-Amino acids on heating give piperazine (cyclic diamide).

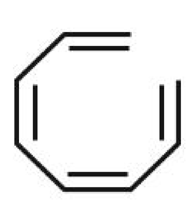
41. The following two ractions are given below.

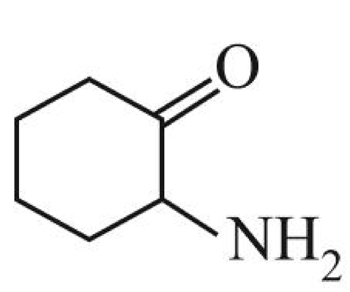
I. 

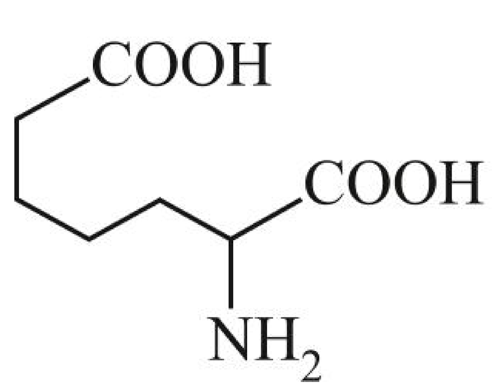
II. 

Select the correct statements.

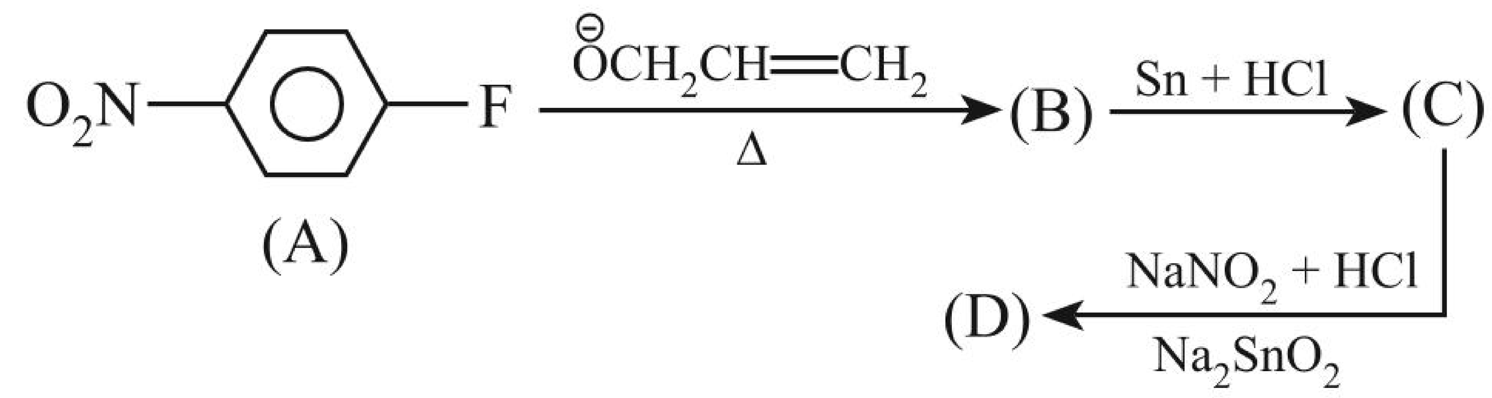
(1) Product (c) is 

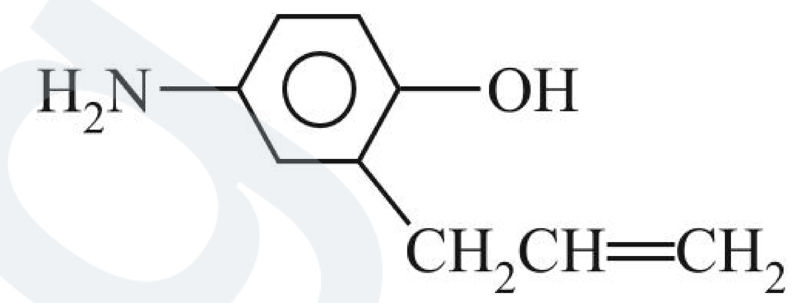
(2) Product (c) is 

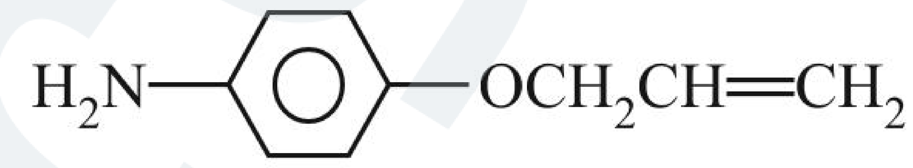
(3) Product (Y) 

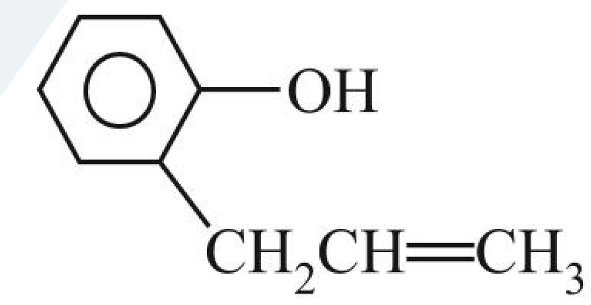
(4) Product (Y) is 

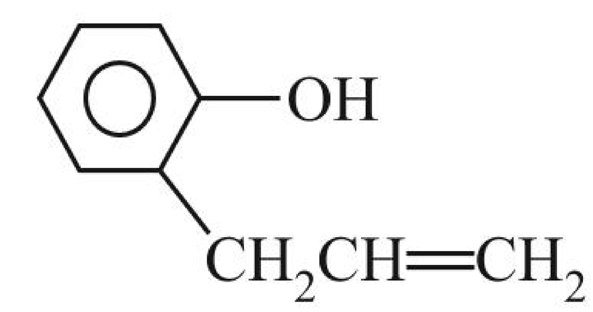
42. Select the correct statements for the reacton given below:



(1) Product (C) is 

(2) Product (C) is 

(3) Product (D) is 

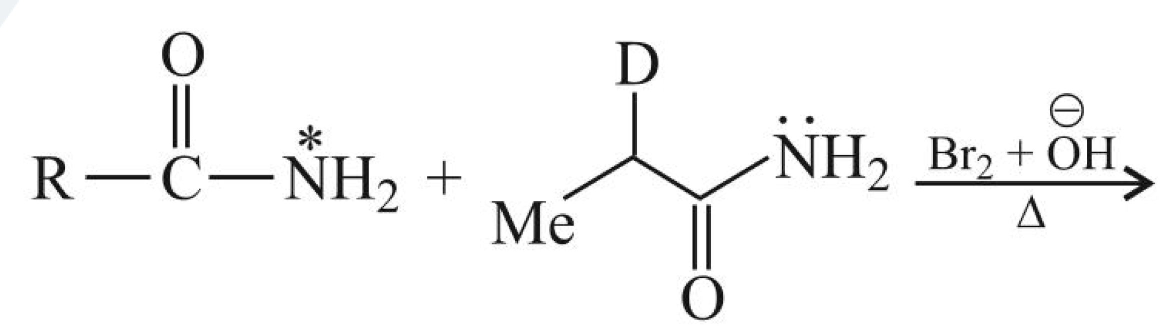
(4) Product (D) is 

43. Which of the following will give Hofmann-Bromamide reaction?

(1) CH_3CONH_2 (2) $PhCONH_2$

(3) $PhCONH{-}Ph$ (4) $CH_3CPNHBr$

44. Which statements are correct about the reaction?



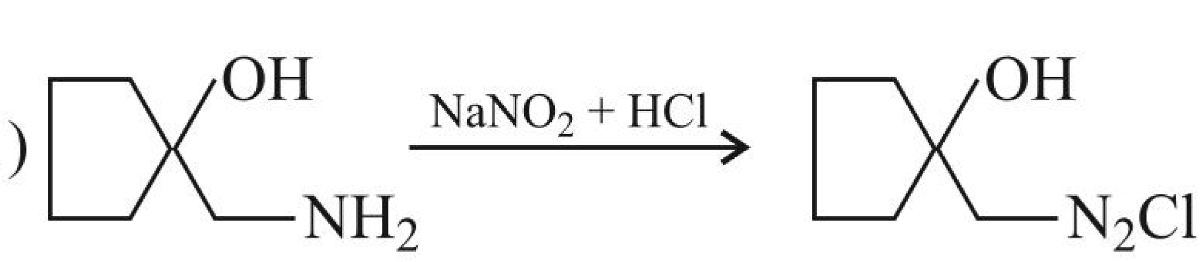
(1) A mixture of two amines is formed, which suggests that rearrangement is intramolecular.

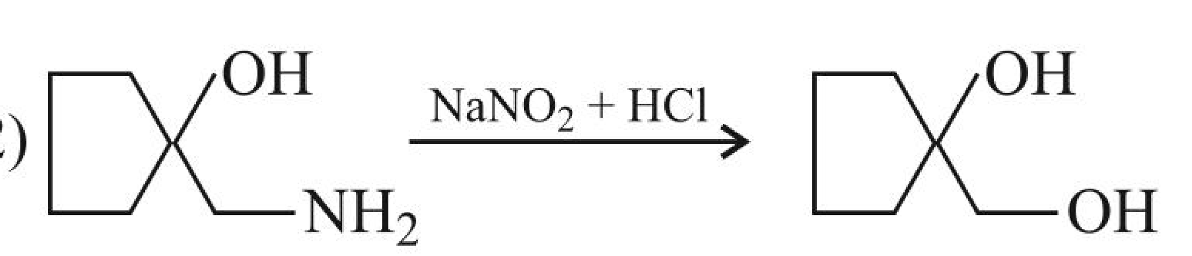
(2) If R is chiral, it migrates with retention of configuration.

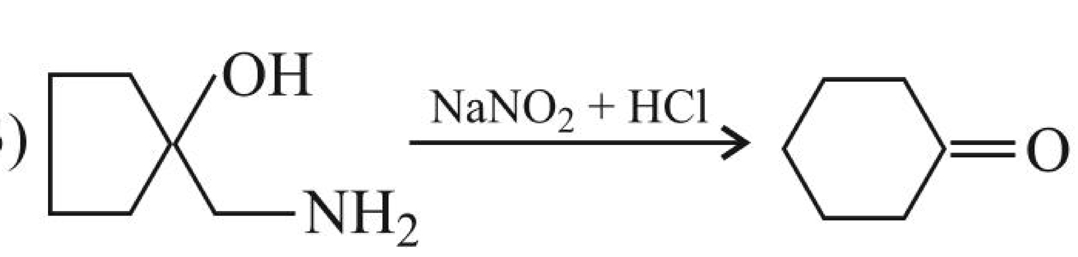
(3) A mixture of four different amines is formed, which suggests that a free acyl nitrene $\left[R-\overset{O}{\overset{\|}{C}}-\ddot{N}:\right]$ intermediate is formed.

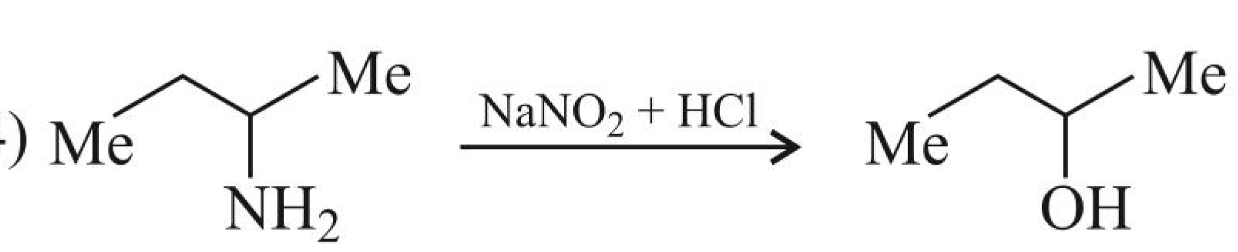
(4) A mixture of two different amines and a free acyl nitrene intermediate is formed.

45. Which of the following reactions are correct?

(1) 

(2) 

(3) 

(4) 

Optically active Optically inactive

46. Which of the following reactions are correct?

(1) $CH_3CH_2NO_2 \xrightarrow{NaOH} [CH_3-\overset{\ominus}{C}H-NO_2]\overset{\oplus}{Na} \xrightarrow{H_2SO_4} CH_3CHO + NaNO_3$

(2) $CH_3-\underset{NO_2}{\underset{|}{C}H}-C_2H_5 \xrightarrow{NaOH} \left[CH_3-\underset{NO_2}{\underset{|}{\overset{\ominus}{C}}}-C_2H_5\right]\overset{\oplus}{Na} \xrightarrow{H_2SO_4} CH_3-\underset{O}{\underset{\|}{C}}-C_2H_5 + NaNO_3$

(3) $CH_3CH_2NO_2 \xrightarrow{H_2SO_4} CH_3-\overset{O}{\overset{\|}{C}}-NHOH \xrightarrow{H_2O} CH_3COOH + NH_2OH$

(4) $CH_3-\underset{NO_2}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3 \xrightarrow{HCl}$ No reaction

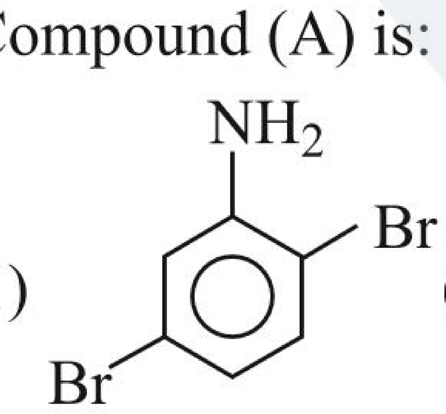
Linked Comprehension Type

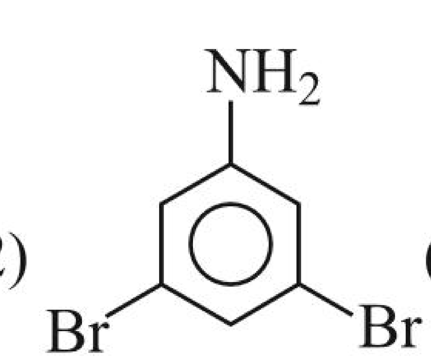
Paragraph 1

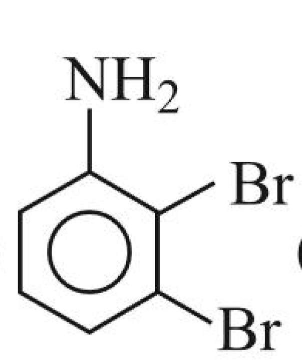
i. Organic compound (A) (Molar mass = 251) (Contains 63.7% of Br) $\xrightarrow{\text{(i) Diazotisation, (ii) } Na_2SnO_2}$ Solid (B) (Contains 67.8% of Br) $\xrightarrow{\text{Nitration}}$ One mono nitro compound

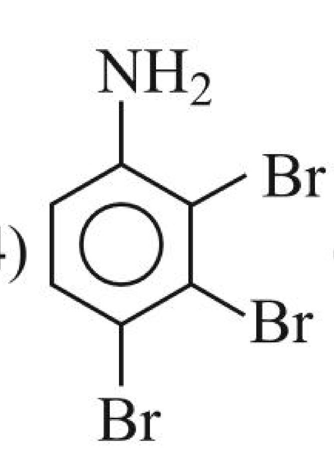
ii. Compound (C) [Isomer of (A)] $\xrightarrow{\text{(i) Diazotisation, (ii) CuBr}}$ Compound (D) (Contains 76.4% of Br) $\xrightarrow{\text{Nitration}}$ One mono nitro compound

1. Compound (A) is:

(1)  (I)

(2)  (II)

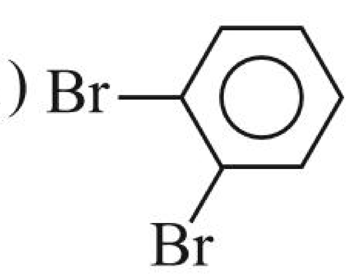
(3)  (III)

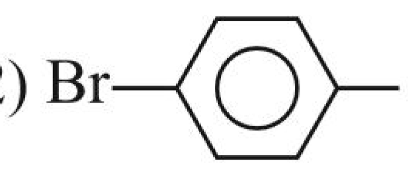
(4)  (IV)

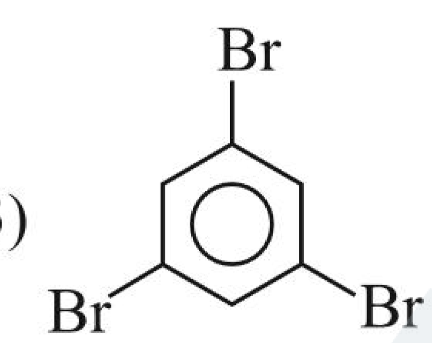
2. Compound (C) is:

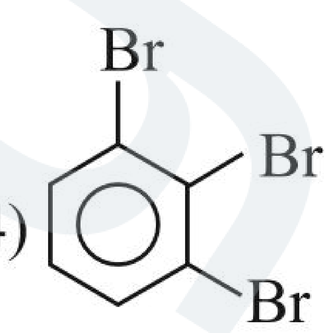
(1) (I) (2) (II)
(3) (III) (4) (IV)

3. Compound (B) is:

(1)  (V)

(2)  (VI)

(3)  (VII)

(4)  (VIII)

4. Compound (D) is:

(1) (V) (2) (VI)
(3) (VII) (4) (VIII)

Paragraph 2

An amino acid reacts with 10 ml 0.05M NaOH and the final solution has pH = 2.30. When 20 ml of the same base is added in the resulting solution, the pH becomes 9.7. Identify the amino acid and calculate the isoelectric point of the amino acid. This amino acid is prepared by the reaction of compound (X) with NH_3 and further hydrolysis with HCN. Compound (X) is less C atom containing compound that gives positive iodoform test and positive Fehling's solution test.

5. Amino acid is:

(1) $H_3C-CH_2-\underset{NH_2}{\underset{|}{CH}}-COOH$

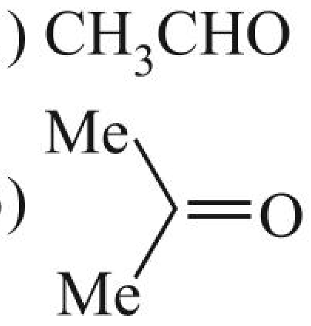
(2) $H_3C-\underset{NH_2}{\underset{|}{CH}}-COOH$

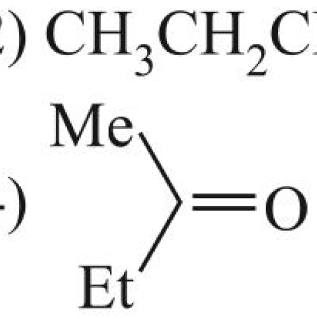
(3) $H_3C-\underset{NH_2}{\underset{|}{CH}}-CH_2-COOH$

(4) $H_2N-CH_2-CH_2-COOH$

6. Compound (X) is:

(1) CH_3CHO (2) CH_3CH_2CHO

(3) 

(4) 

7. Isoelectric point of the amino acid is:

(1) pH = 7.0 (2) pH = 8.0
(3) pH = 6.0 (4) pH = 9.0

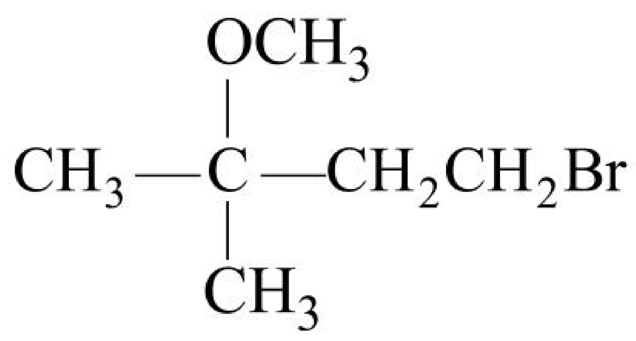
Paragraph 3

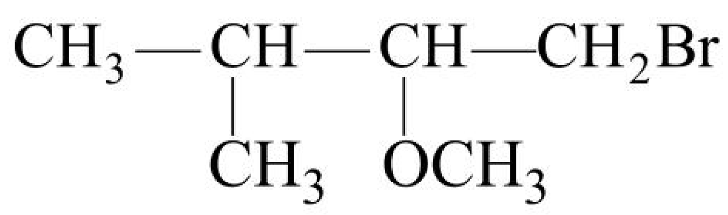
1 mol (A) + NH_3 $\longrightarrow$ 1 mol (B) $\xrightarrow{CH_3I}$ (C)
Alkyl bromide

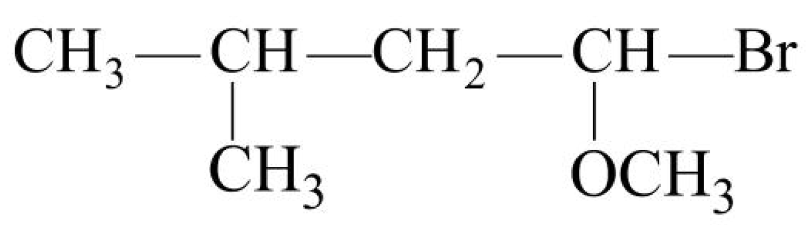
(B) $\xrightarrow{HNO_2}$ (D) $\xrightarrow{\text{Oxidation and decarboxylation}}$ 2-Methoxy-2-methyl propane

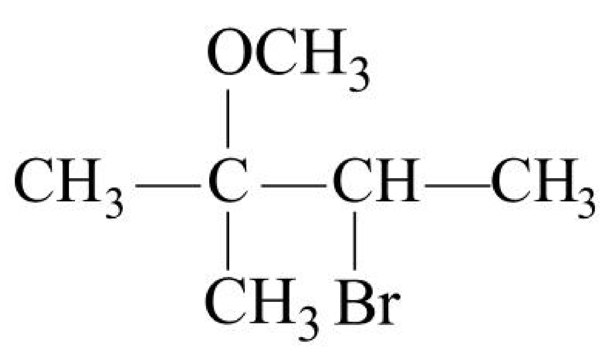
(C) $\xrightarrow{HNO_2}$ (E)

8. Compound (A) is:

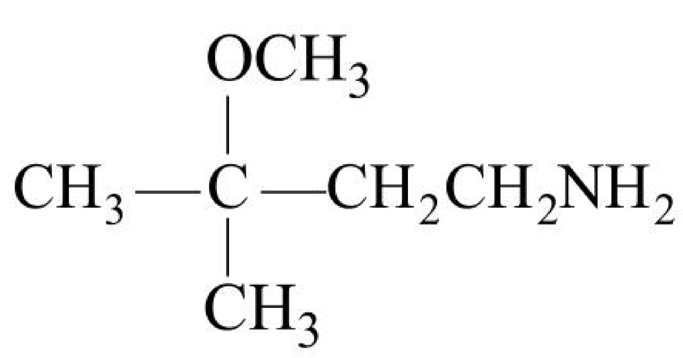
(1) 

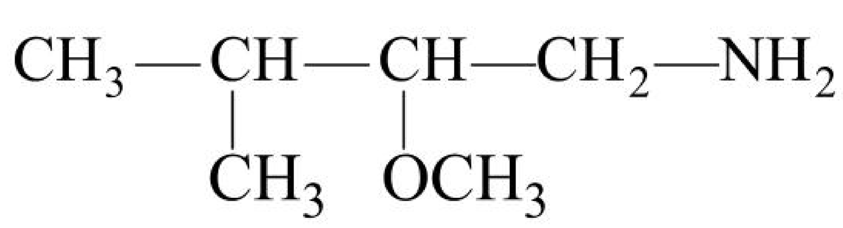
(2) 

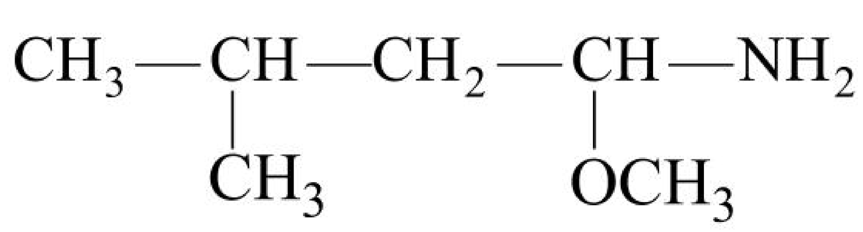
(3) 

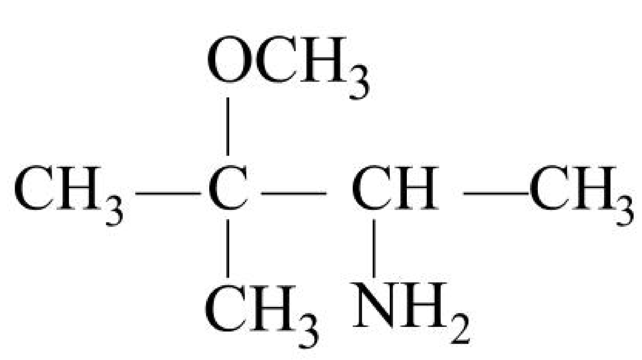
(4) 

9. Compound (B) is:

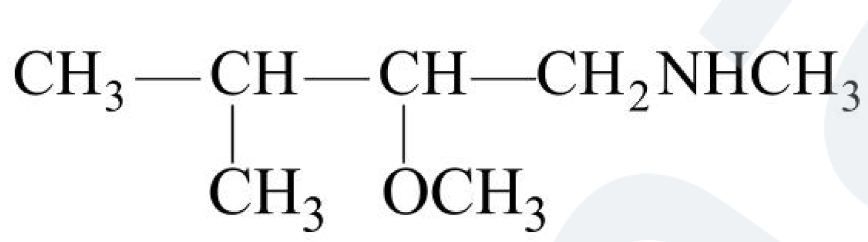
(1) 

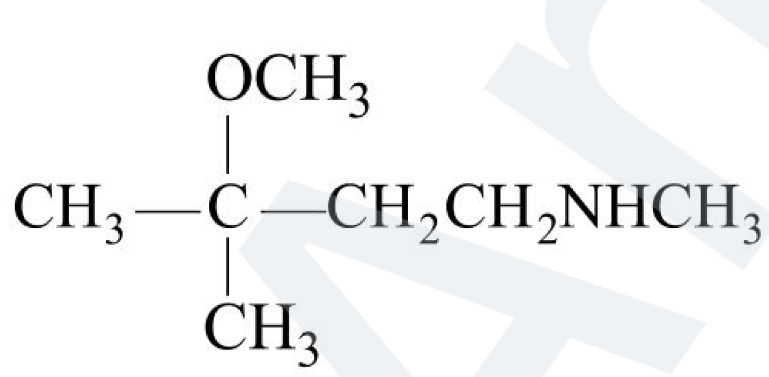
(2) 

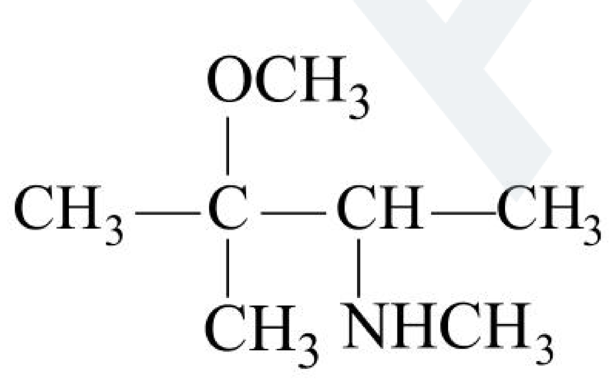
(3) 

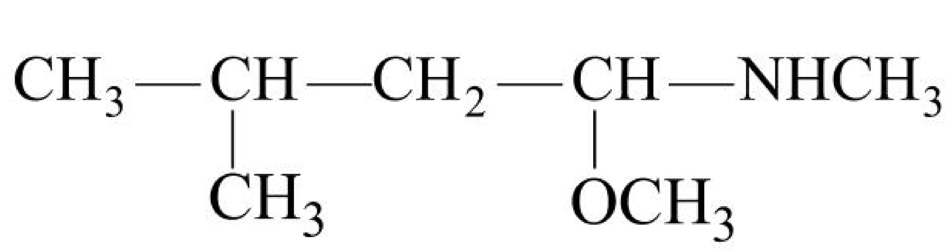
(4) 

10. Compound (C) is:

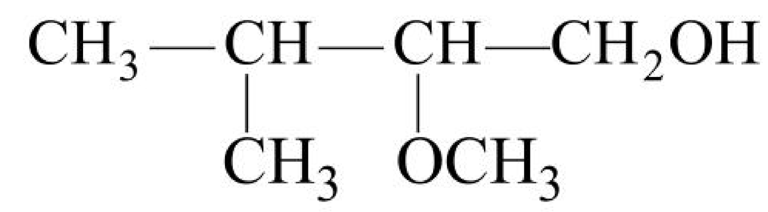
(1) 

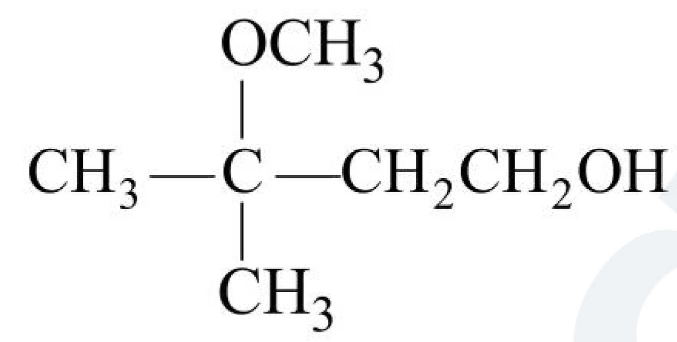
(2) 

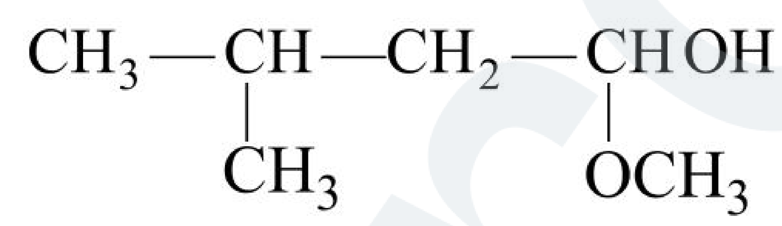
(3) 

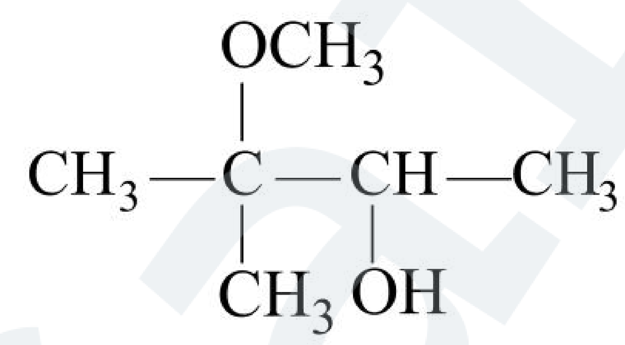
(4) 

11. Compound (D) is:

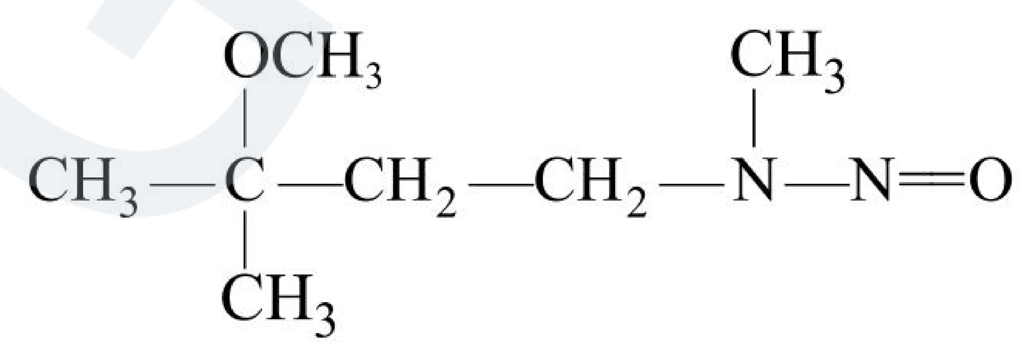
(1) 

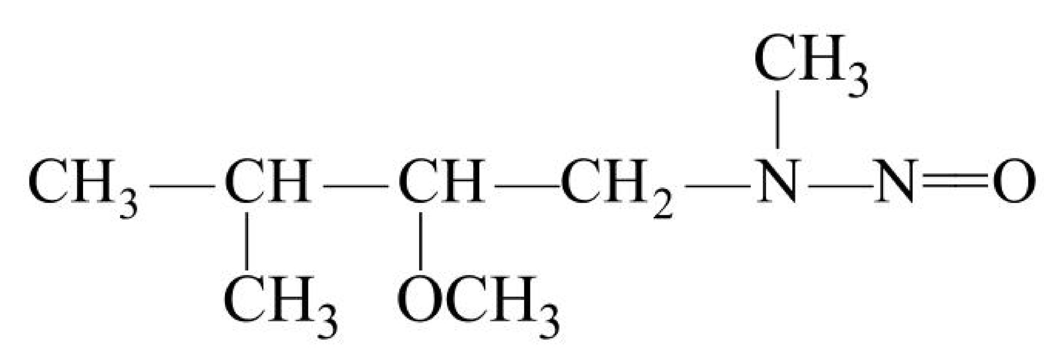
(2) 

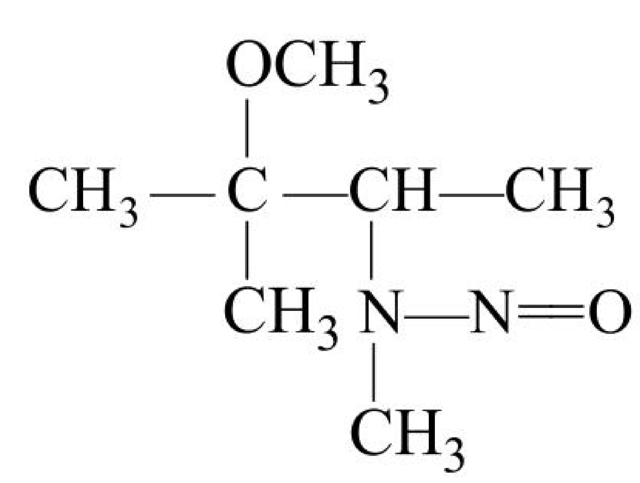
(3) 

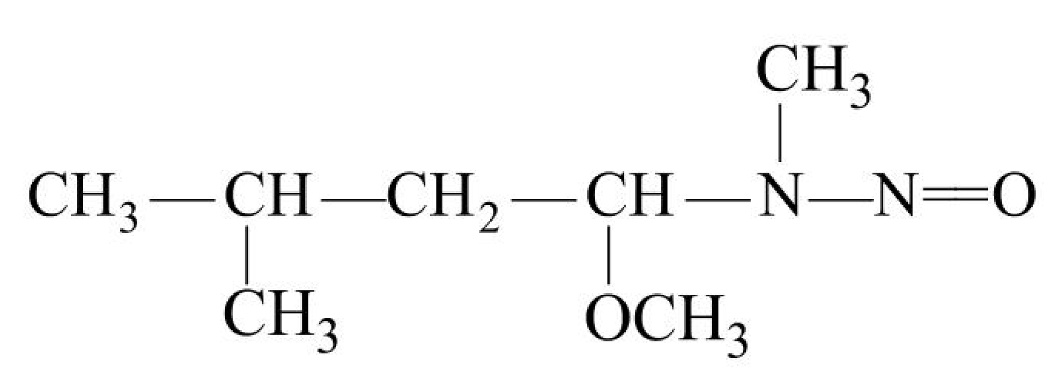
(4) 

12. Compound (E) is:

(1) 

(2) 

(3) 

(4) 

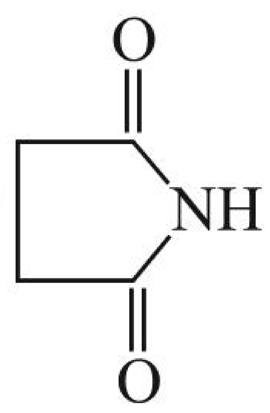
Paragraph 4

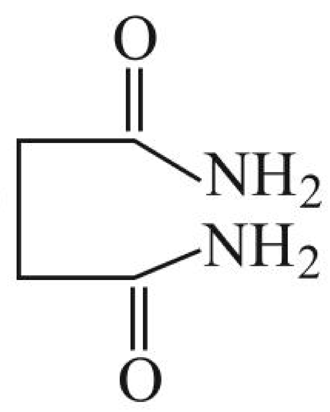
A substance (X) contains 41.37% C, 6.89% H. 0.116 gm of (X) gave NH_3, which was absorbed in 50 ml of N/10 H_2SO_4. The excess of acid required 30 ml of N/10 NaOH for neutralisation. (X) on treatment with HNO_2 gave succinic acid. (X) on heating lost NH_3 to give (A). (A) reacts with Br_2 and NaOH to give (B) containing 41.02% C, 5.88% H, and 11.96% N. (B) on further treatment with Br_2 and NaOH gives (C) (3-amino propanoic acid). (C) reacts with HNO_2 to give β-hydroxy-propanoic acid.

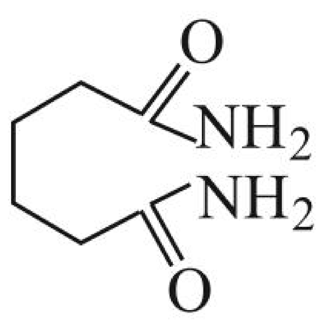
13. Percentage of N in (X) is:

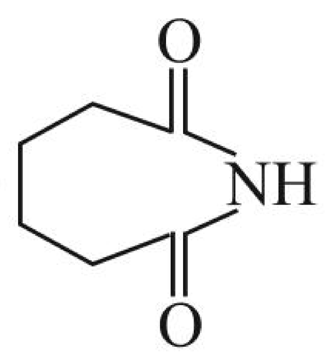
(1) 34.38% (2) 24.38%
(3) 14.38% (4) 44.48%

14. Compound (X) is:

(1)  (I)

(2)  (II)

(3)  (III)

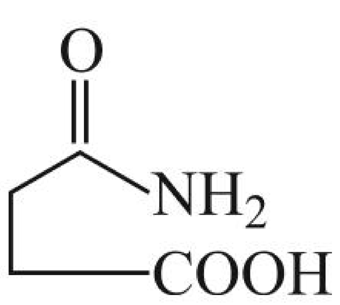
(4)  (IV)

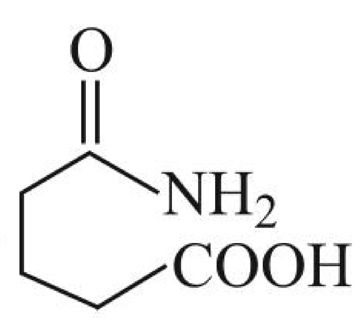
15. Compound (A) is:

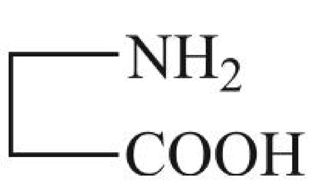
(1) (I) (2) (II)

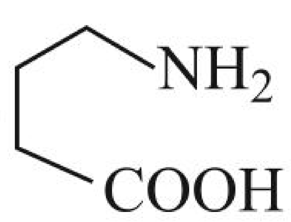
(3) (III) (4) (IV)

16. Compound (B) is:

(1) 
(V)

(2) 
(VI)

(3) 
(VII)

(4) 
(VIII)

17. Compound (C) is:

(1) (V) (2) (VI)

(3) (VII) (4) (VIII)

18. The conversion of (B) to (C) is called:

(1) Hofmann ammonolysis

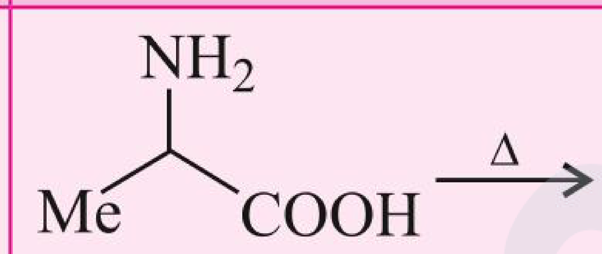
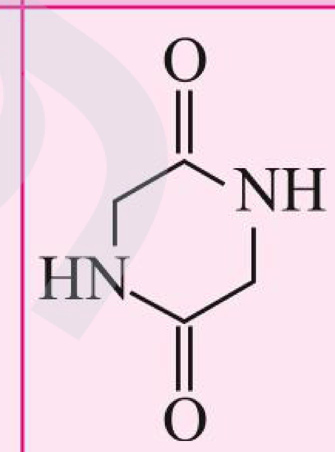
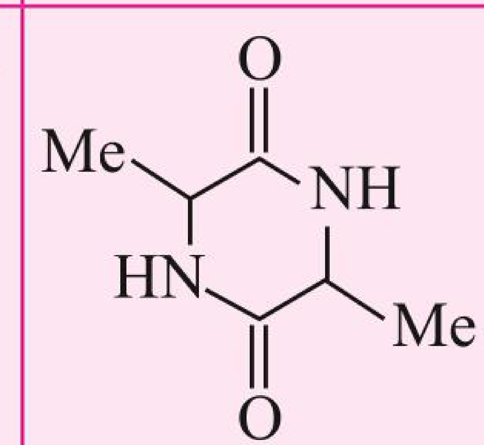
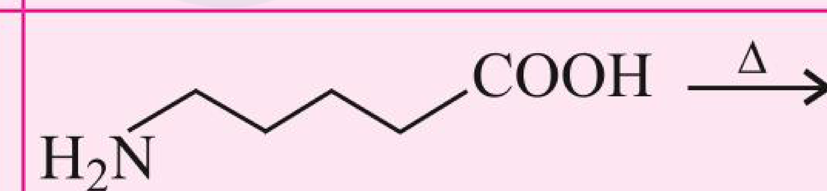
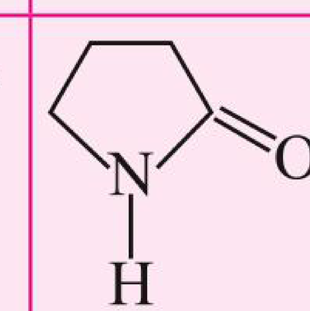
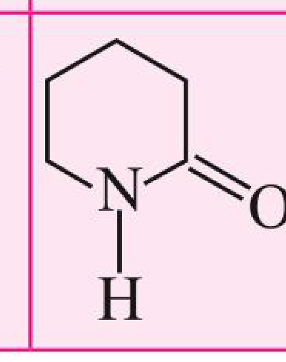
(2) Hofmann bromamide degradation

(3) Lossen rearrangement

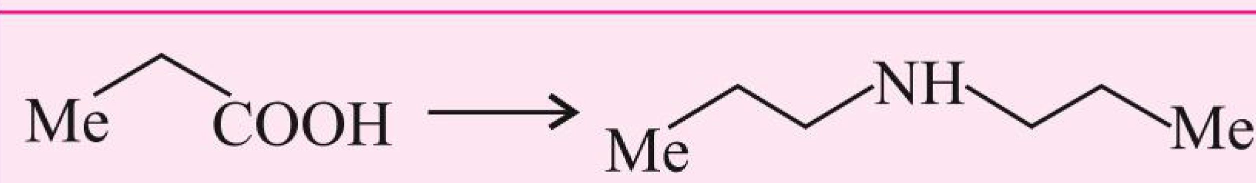
(4) Curtius rearrangement

Matrix Match Type

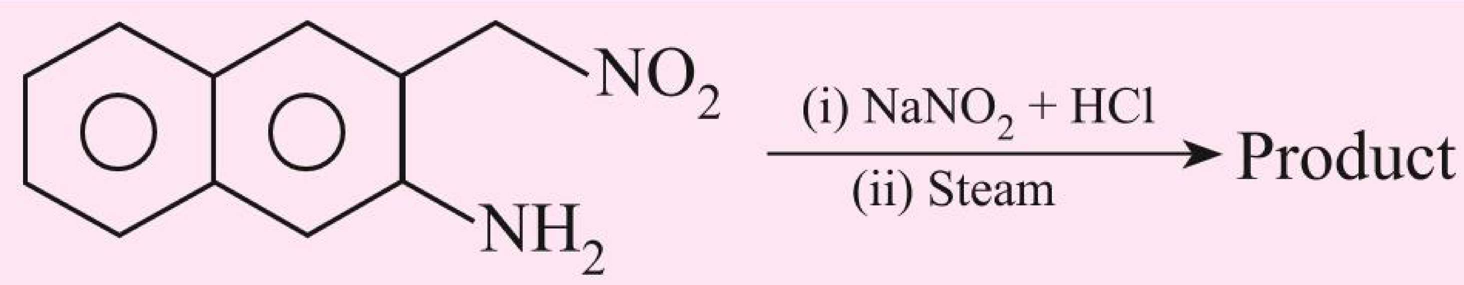
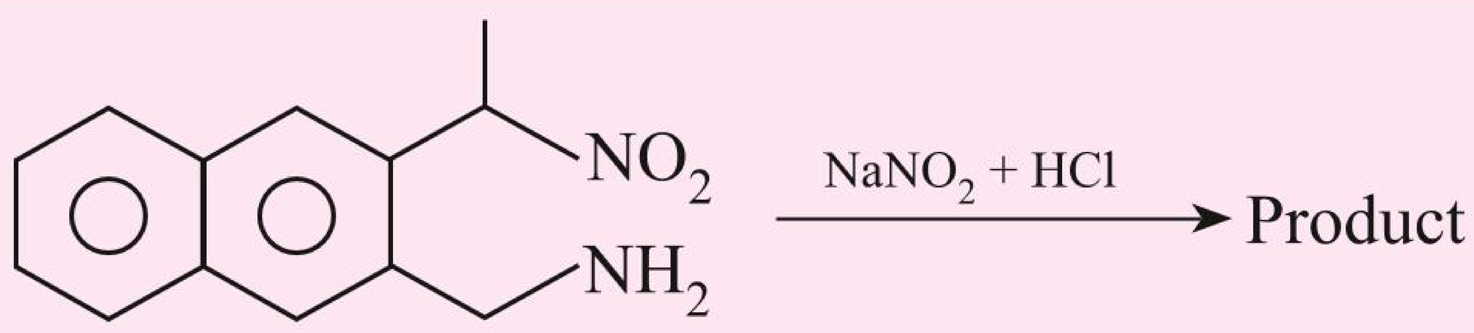
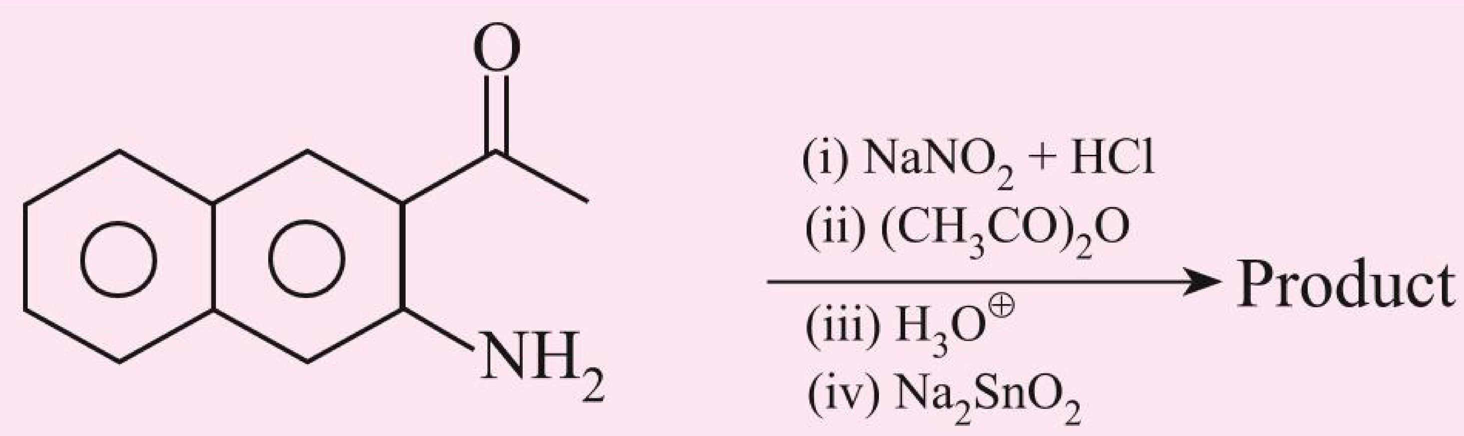
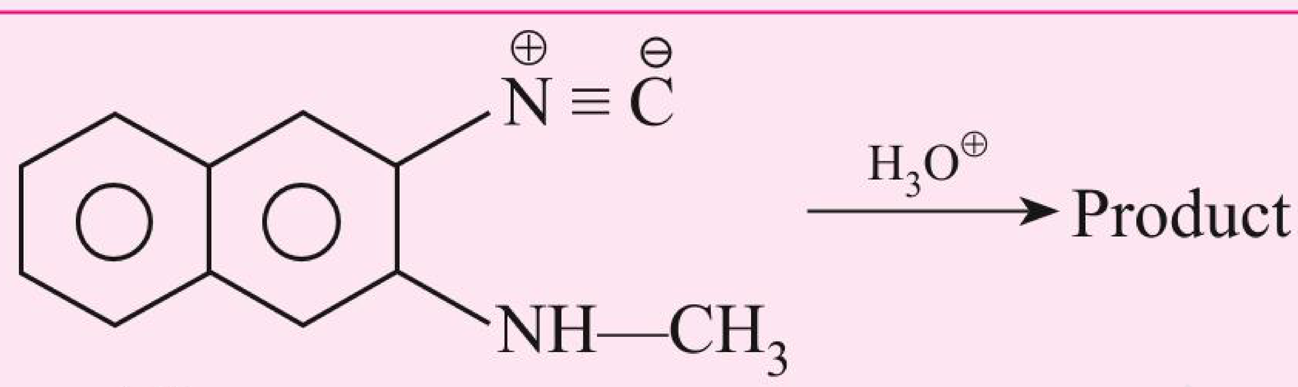
1.

S. No.	Column I Compound		Column II Product
a.		**p.**	
b.	$H_2N—CH_2—COOH \xrightarrow{\Delta}$	**q.**	
c.		**r.**	Three stereoisomers
d.		**s.**	
		t.	

2.

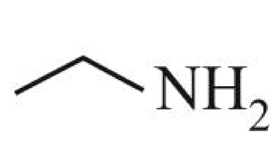
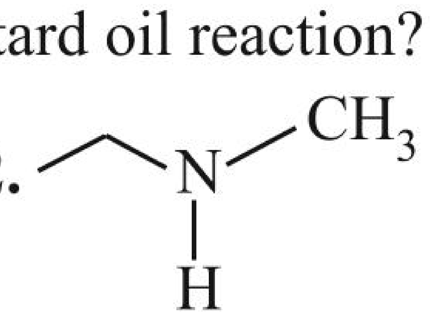
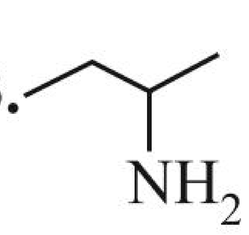
S.No.	Column I Reaction		Column II Reagents
a.		**p.**	(1) $SOCl_2$ (2) NH_3 (3) Br_2 + $NaOH/H_2O$
b.		**q.**	(1) LAH (2) PBr_3 (3) Li+ CuI (4) C_2H_5COCl (5) NH_3 (6) H_2/Ni
c.		**r.**	(1) LAH (2) PBr_3 (3) KCN (4) LAH
d.		**s.**	(1) $SOCl_2$ (2) NH_3 (3) LAH
e.		**t.**	(1) $SOCl_2$ (2) $C_3H_7NH_2$ (3) LAH
f.		**u.**	(1) $SOCl_2$ (2) H_2 + Pd + $BaSO_4$ (3) $C_2H_5NH_2$ (4) H_2 + Ni

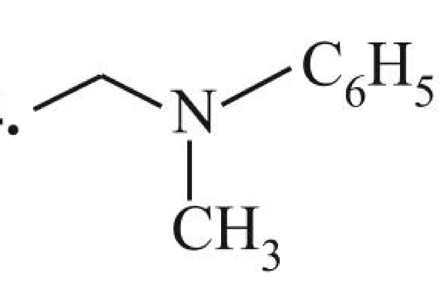
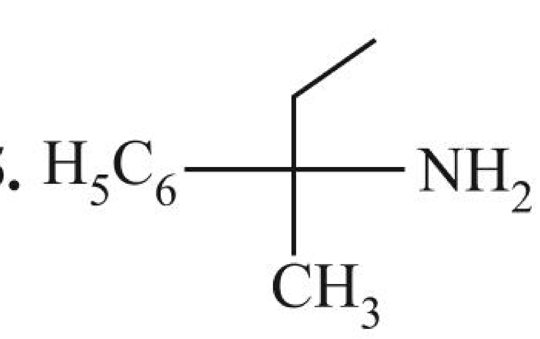
3. Match the items given in column I with that in column II and III.

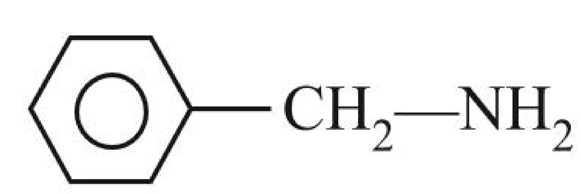
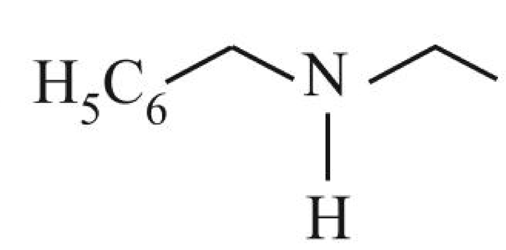
	Column I		Column II		Column III
	Reactions		**Test for reactants**		**Test for products**
a	 (A)	**i**	Carbylamine test	**p**	Gives colour with neutral $FeCl_3$ solution.
b	 (B)	**ii**	Dye test	**q**	Gives CAN test
c	 (C)	**iii**	Brady's reagent test	**r**	Gives blood red colour with NaOH
d	 (D)	**iv**	Libermann's nitroso reaction test	**s**	Gives blue colour with NaOH
				t	$NaHCO_3$ test

Numerical Value Type

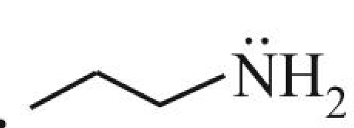
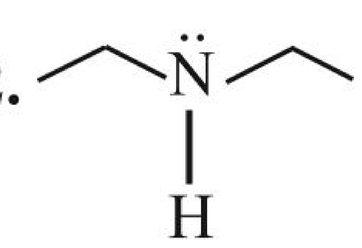
1. When α-amine propanoic acid is heated, how many isomeric piperazines (including stereoisomers are obtained).
2. When β-aminobutanoic acid is heated how many diastereomers are obtained
3. How many compounds of the following gives cyclic amides on heating
   I. 4-aminobutanoic acid
   II. 4-amino pentanoic acid
   III. 5-amino pentanoic acid
   IV. 5-amino hexanoic acid
   V. 2-amino propanoic acid
   VI. 3-amino propanoic acid
4. In the Q. No. 3 above how many of following compounds will give five membered cyclic amide.
5. In the Q. No. 3 above how many of the following compound will give six membered cyclic amide.
6. Of the following amines how many can be separated by Hoffmann's mustard oil reaction?

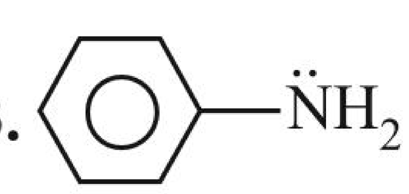
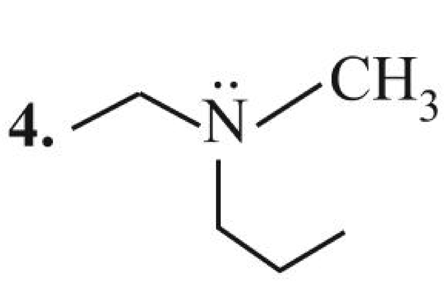
1.  **2.**  **3.** 

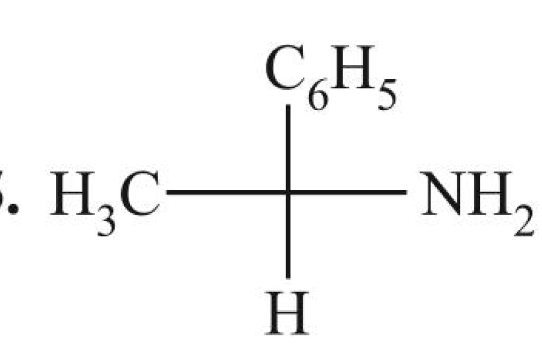
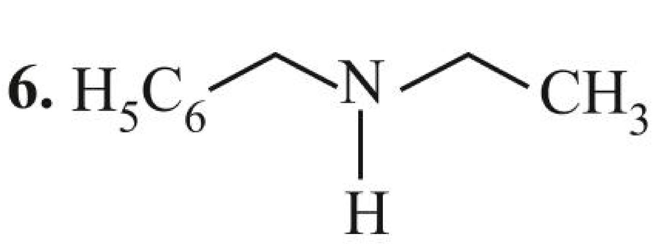
4.  **5.** 

6.  **7.** 

7. Of the following amines, how many can give carbylamine reaction?

1.  **2.** 

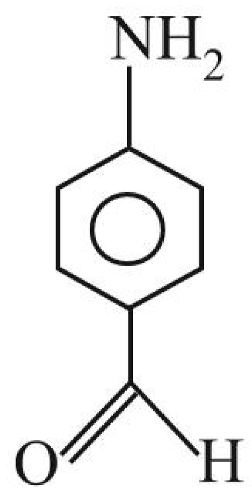
3.  **4.** 

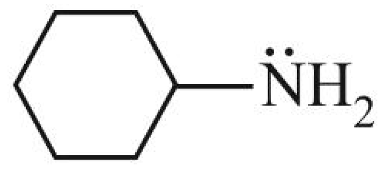
5.  **6.** 

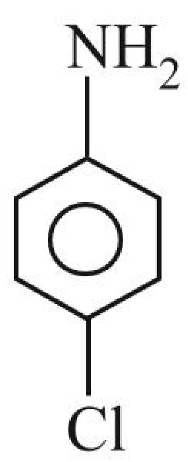
8. $C_6H_5 - NH_2 \xrightarrow[0^{\circ}\text{-}5^{\circ}C]{NaNO_2/HCl} \xrightarrow[\text{dil.HCl}]{C_6H_5\text{–}NH_2} (X)$

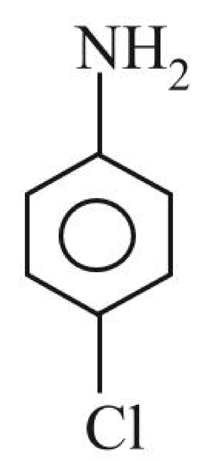
   Find the sum of number of nitrogen atoms present in (X).

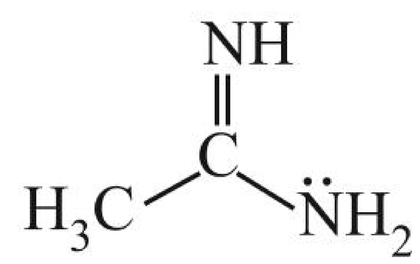
9. Identify how many compounds are more basic than aniline.

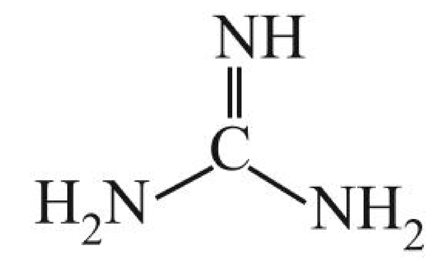
1. 

2 

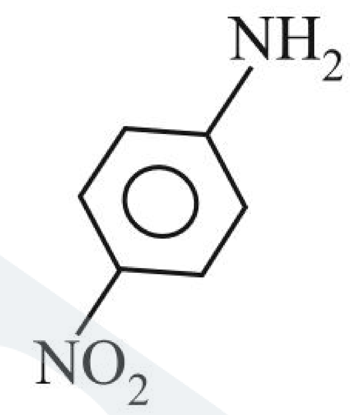
3. 

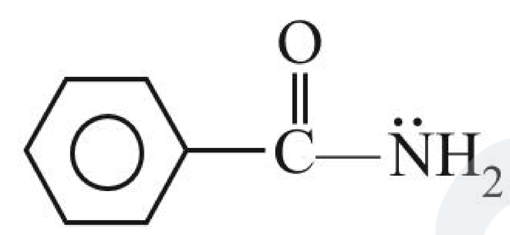
4. 

5. 

6. 

7. 

8. 

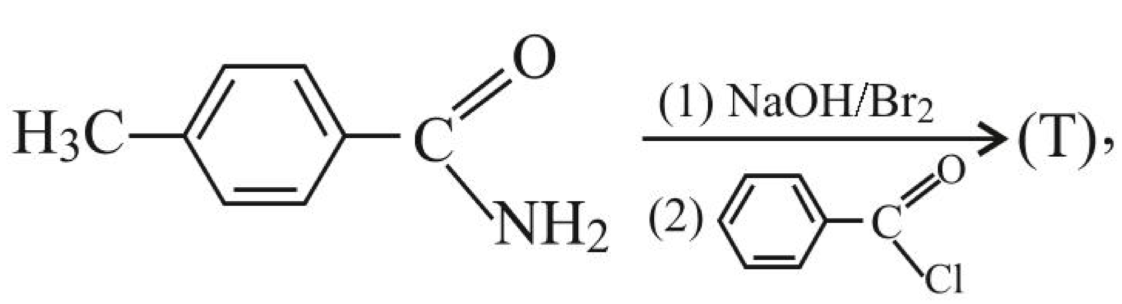
9. 

Archives

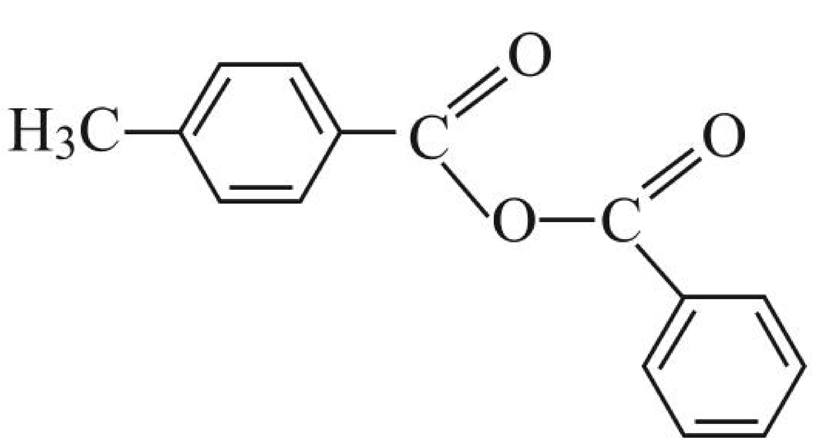
JEE Advanced

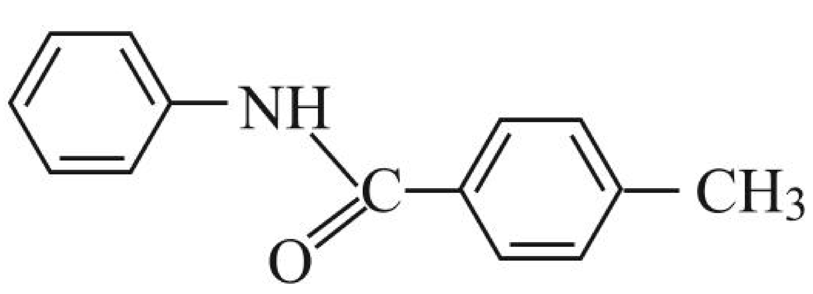
Single Correct Answer Type

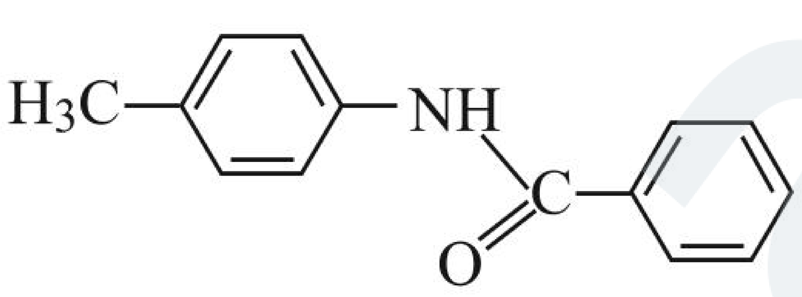
1. In the reaction

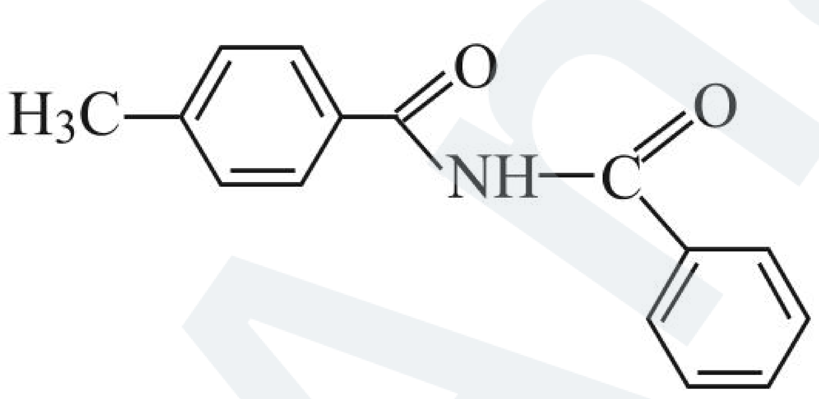


, the structure of the product (T) is:

(1) 

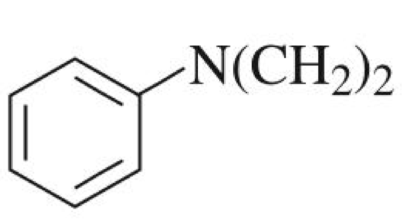
(2) 

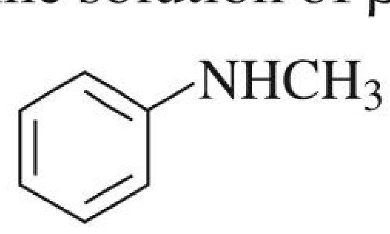
(3) 

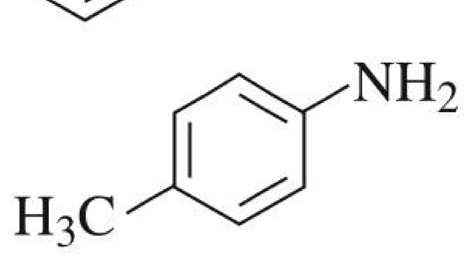
(4) 

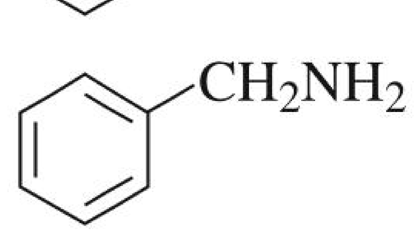
(IIT-JEE 2010)

2. Amongst the compounds given, the one that would form a brilliant colored dye on treatment with $NaNO_2$ in dil. HCl followed by addition to an alkaline solution of β-naphthol is

(1) 

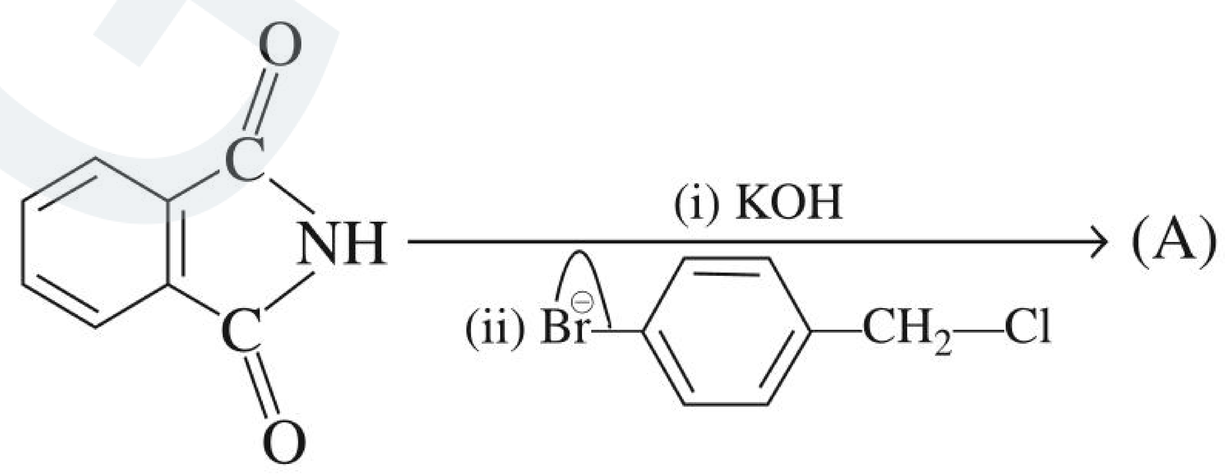
(2) 

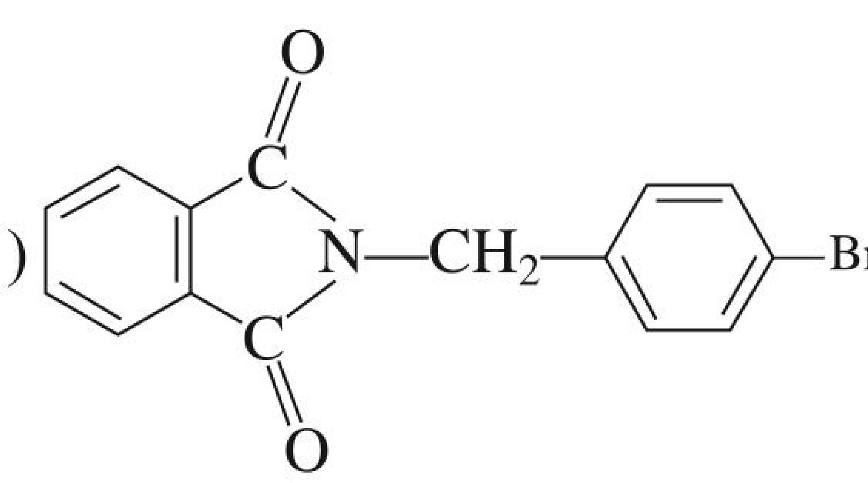
(3) 

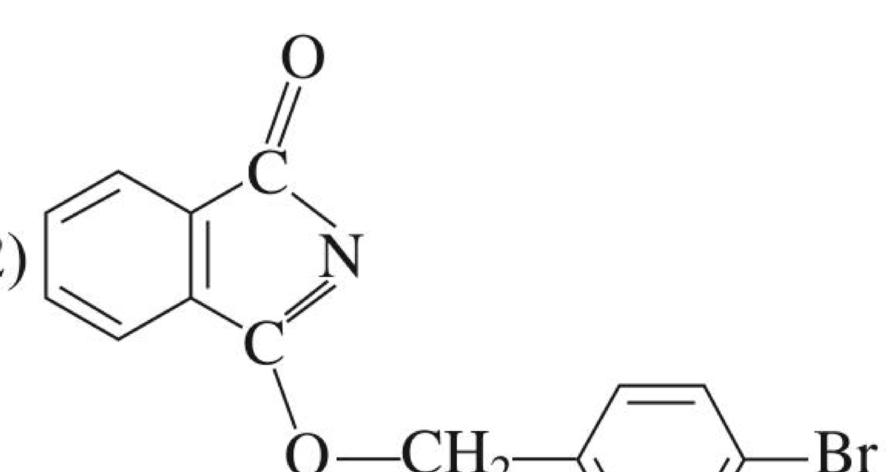
(4) 

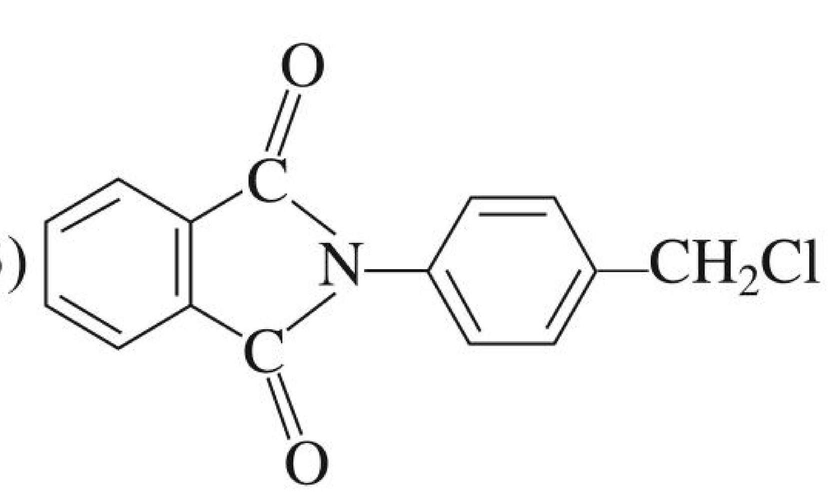
(IIT-JEE 2011)

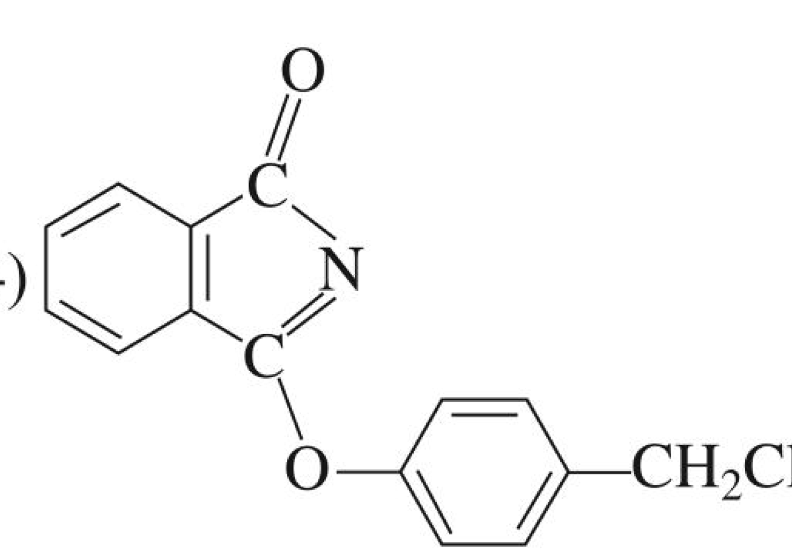
3. The major product of the following reaction is



(1) 

(2) 

(3) 

(4) 

(IIT-JEE 2011)

4. The gas leaked from a storage tank of the Union Carbide plant in Bhopal gas tragedy was:

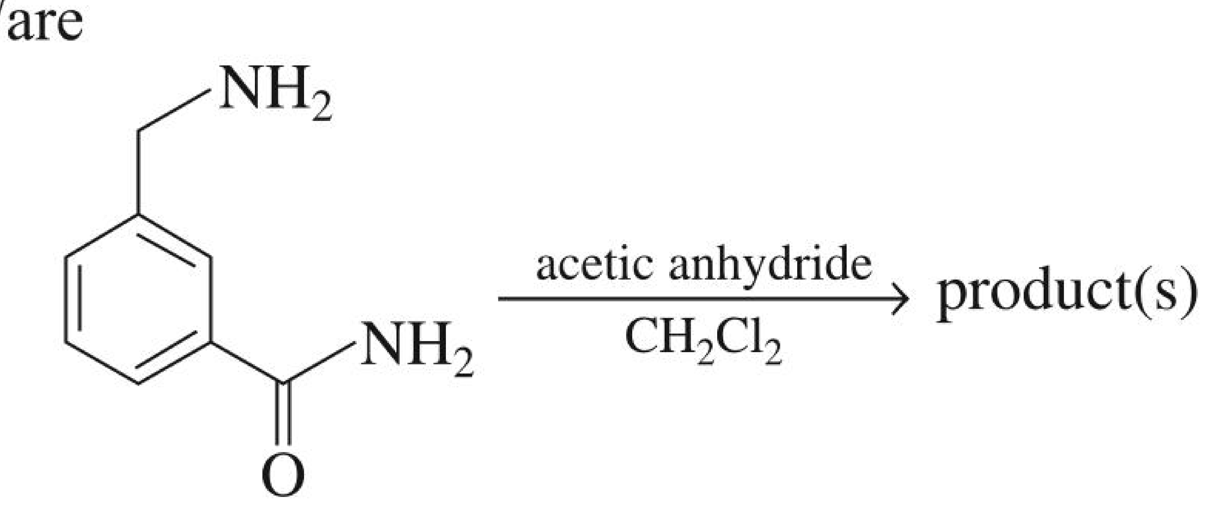
(1) Methylamine
(2) Ammonia
(3) Phosgene
(4) Methylisocyanate

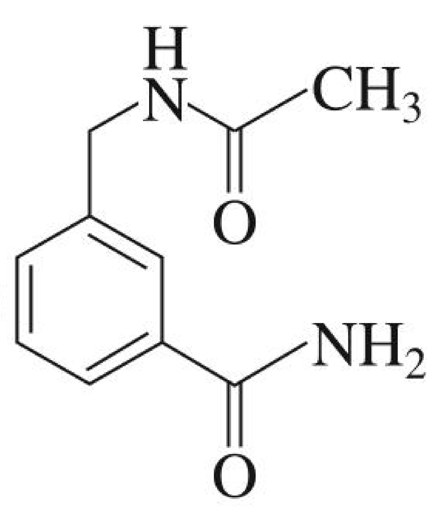
(IIT-JEE 2013)

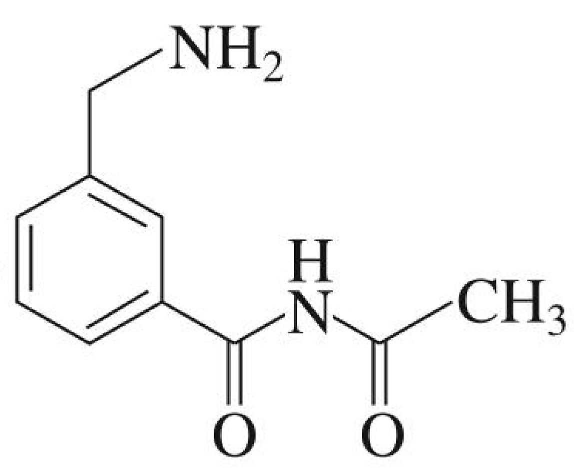
5. On heating an aliphatic primary amine with chloroform and ethanolic potassium hydroxide, the organic compound formed is:
(1) an alkyl cyanide (2) an alkyl isocyanide
(3) an alkanol (4) an alkanediol
(JEE Advanced 2014)

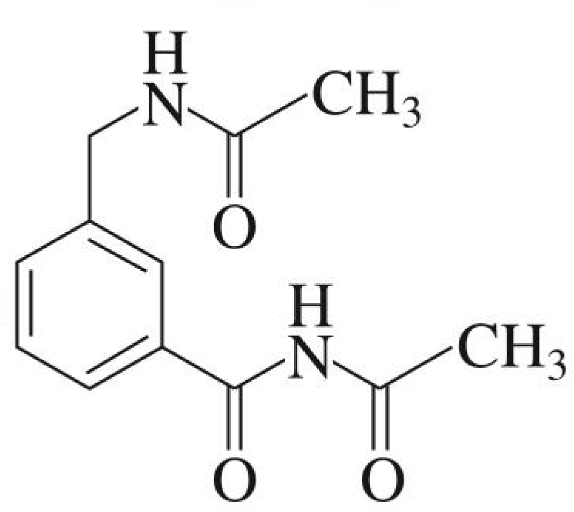
6. For the identification of β-naphthol using dye test, it is necessary to use
(1) dichloromethane solution of β-naphthol.
(2) acidic solution of β-naphthol.
(3) dichloromethane solution of β-naphthol.
(4) dichloromethane solution of β-naphthol.
(JEE Advanced 2014)

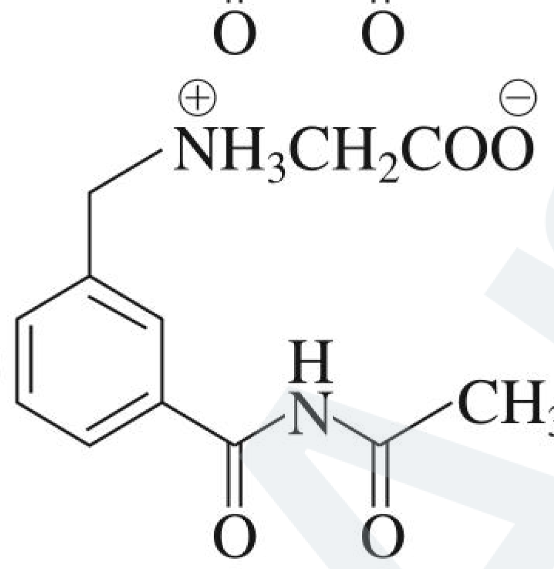
7. In the reaction shown below, the major product(s) formed is/are



(1)  + CH_3COOH

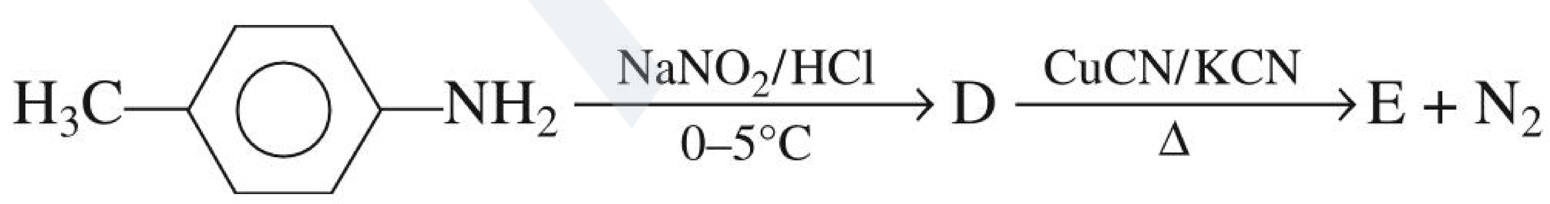
(2)  + CH_3COOH

(3)  + H_2O

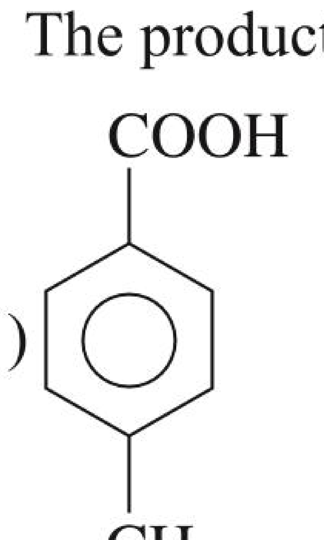
(4) 

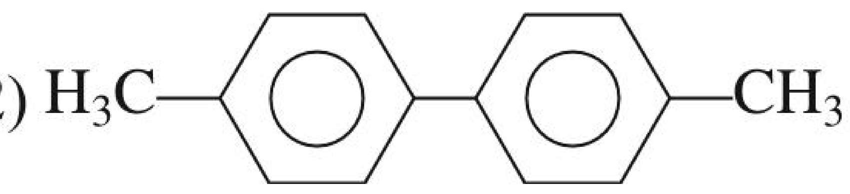
(JEE Advanced 2014)

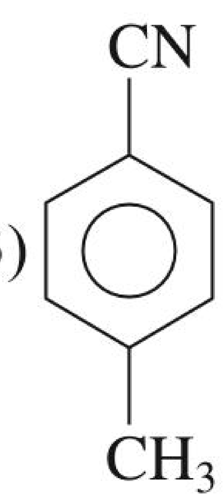
8. In the reaction:

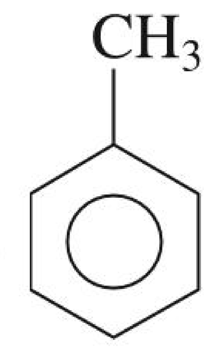


The product (E) is:

(1) 

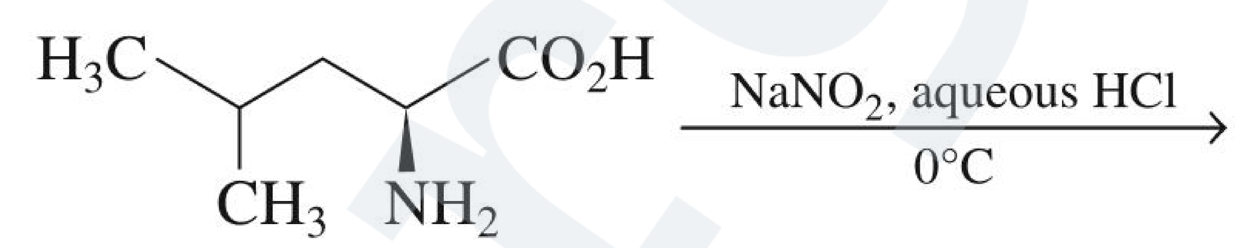
(2) 

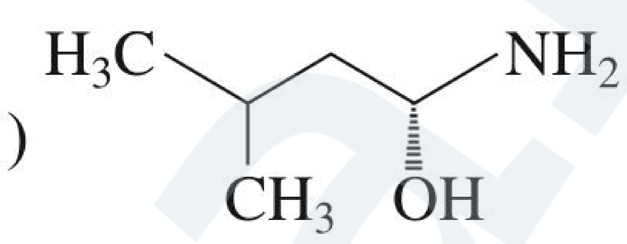
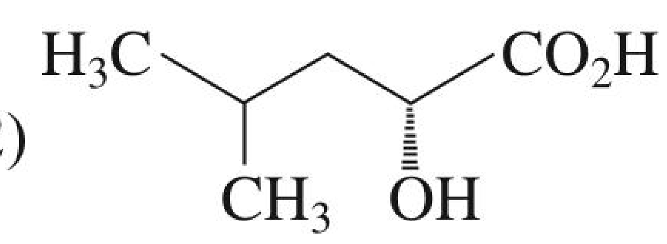
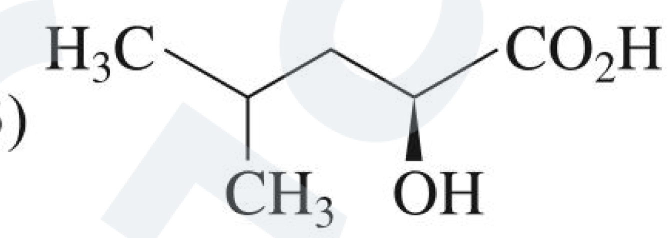
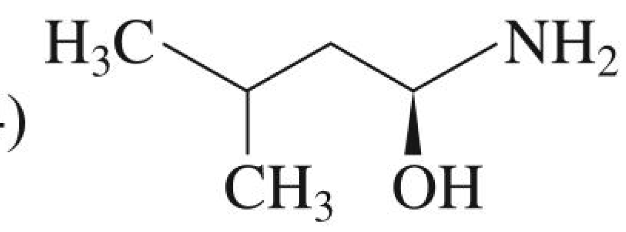
(3) 

(4) 

(JEE Advanced 2015)

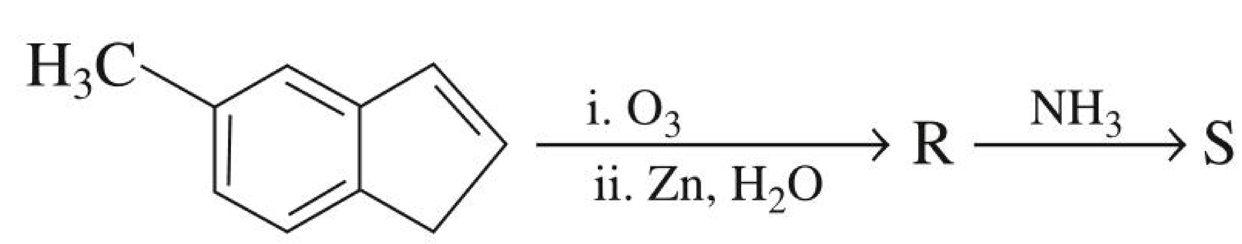
9. The major product of the reaction is

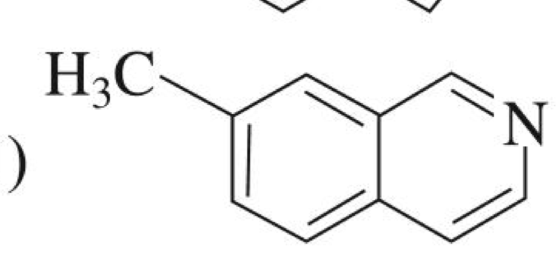
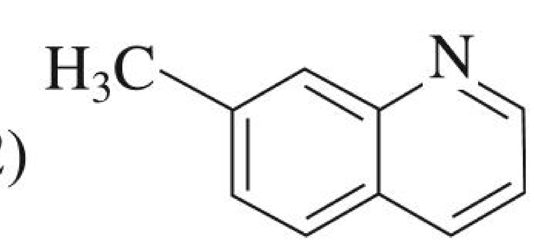
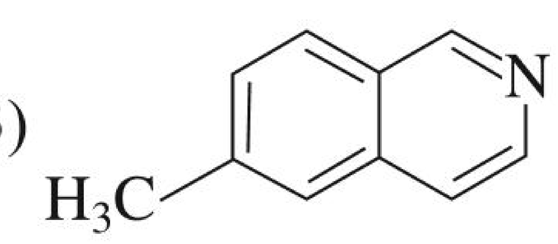
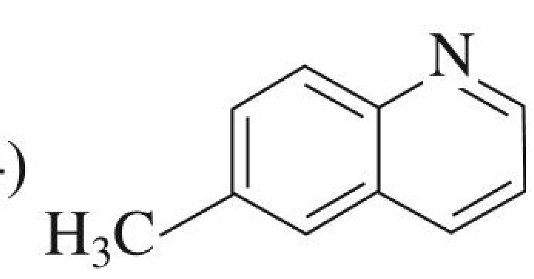


(1) 
(2) 
(3) 
(4) 

(JEE Advanced 2015)

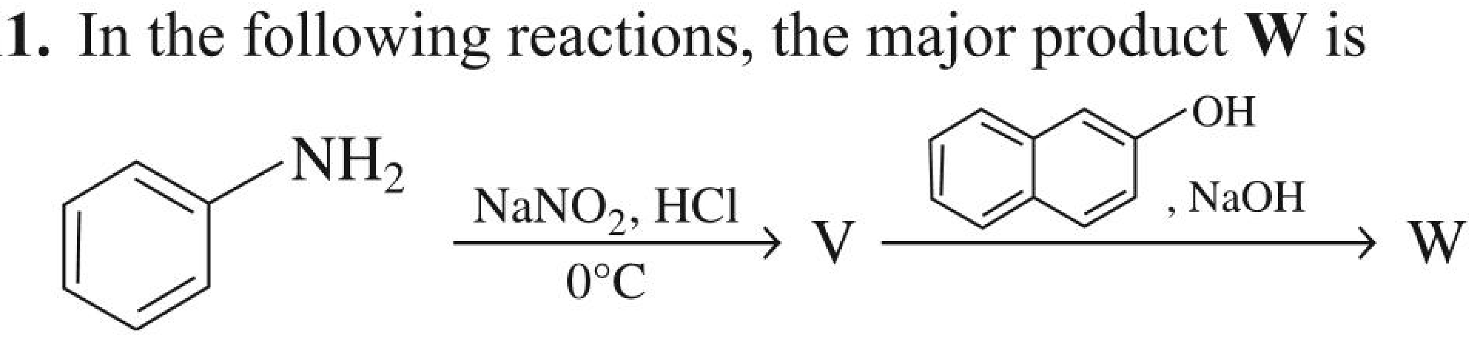
10. In the following reactions, the product S is

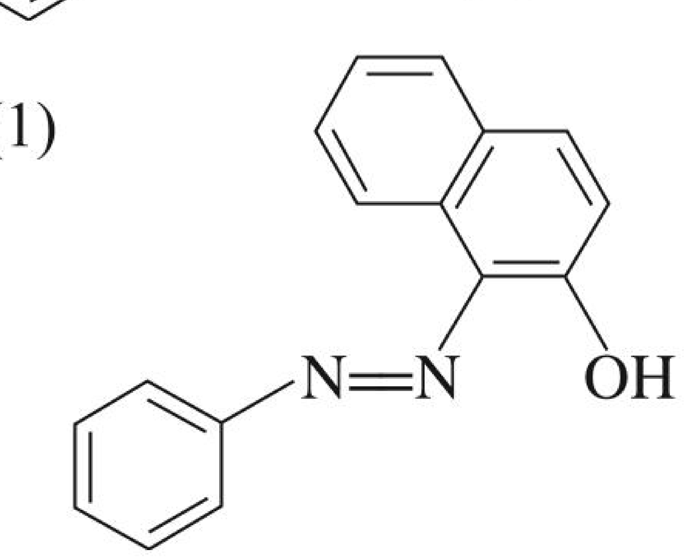


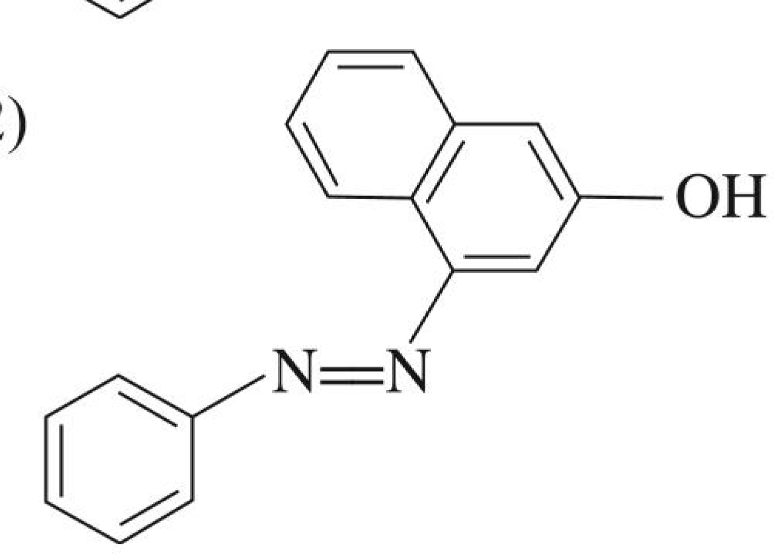
(1) 
(2) 
(3) 
(4) 

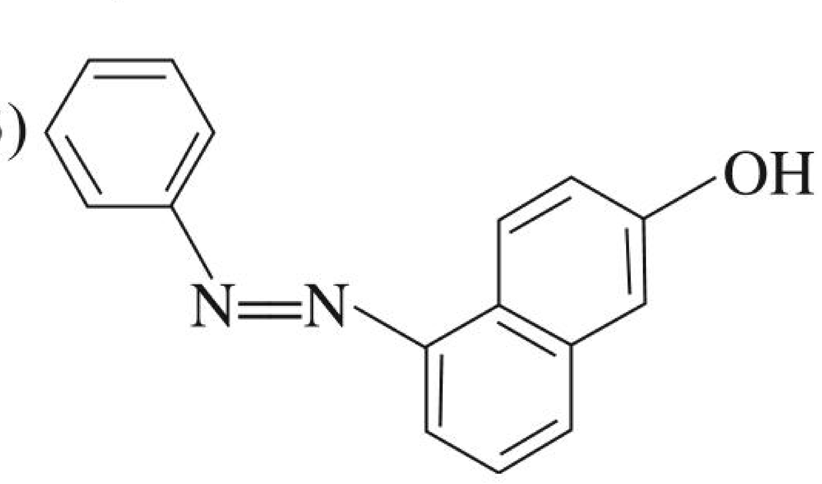
(JEE Advanced 2015)

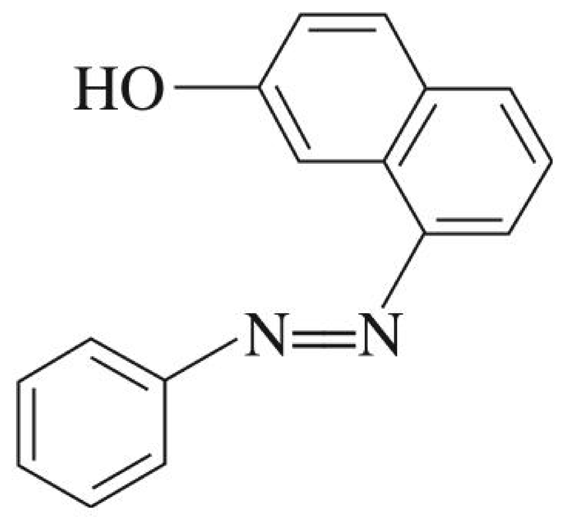
11. In the following reactions, the major product **W** is



(1) 

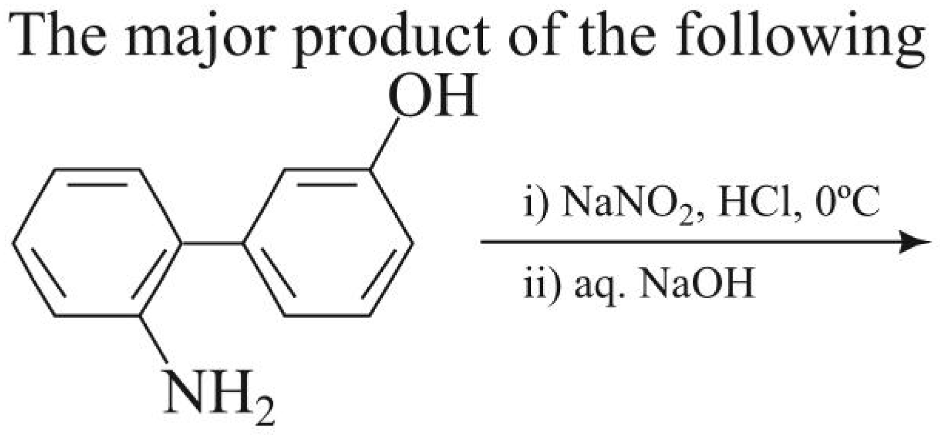
(2) 

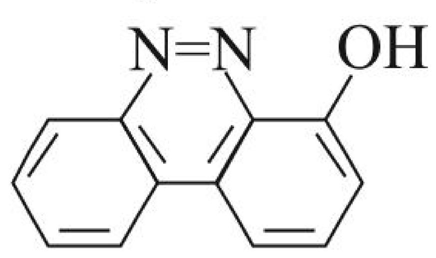
(3) 

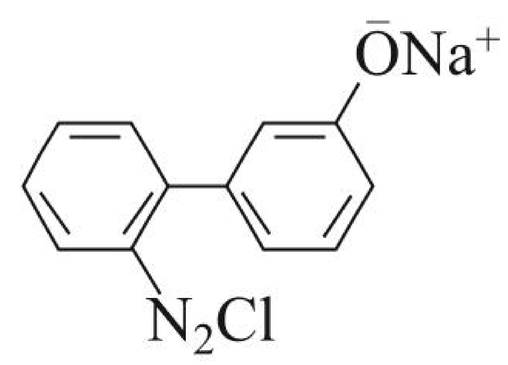
(4) 

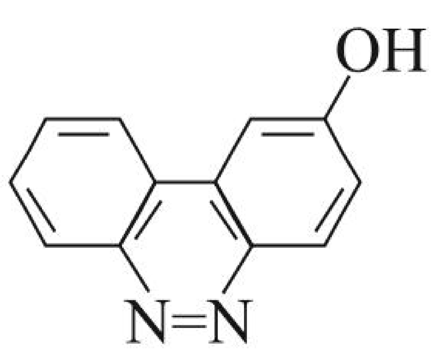
(JEE Advanced 2015)

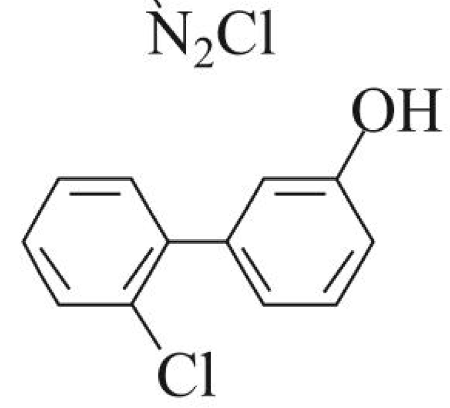
12. The major product of the following reaction is



(1) 

(2) 

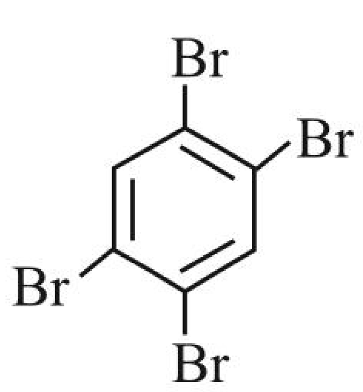
(3) 

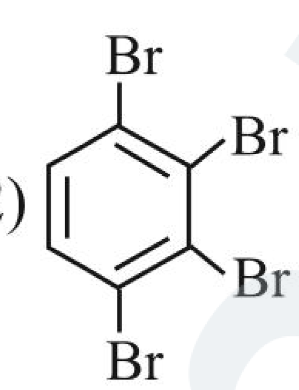
(4) 

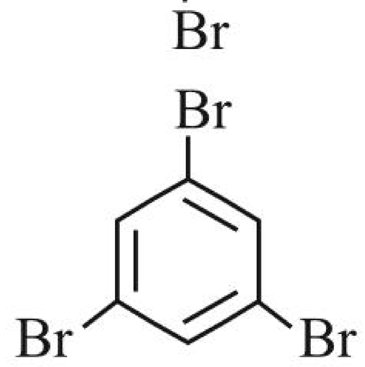
(JEE Advanced 2016)

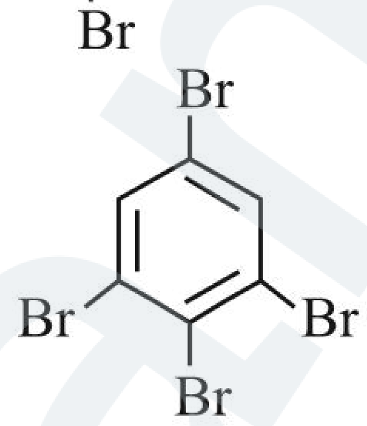
13. Aniline reacts with mixed acid (conc. HNO_3 and conc. H_2SO_4) at 288 K to give P (51%), Q (47%) and R(2%). The major product(s) of the following reaction sequence is (are)

$$R \xrightarrow[\substack{(3)\ H_3O^+ \\ (4)\ NaNO_2,\ HCl/273\text{-}278K \\ (5)\ EtOH,\ \Delta}]{\substack{(1)\ Ac_2O,\ pyridine \\ (2)\ Br_2,\ CH_3CO_2H}} S \xrightarrow[\substack{(3)\ NaNO_2,HCl/273\text{-}278\ K \\ (4)\ H_3PO_2}]{\substack{(1)\ Sn/HCl \\ (2)\ Br_2/H_2O\ (excess)}} \text{major product(s)}$$

(1) 

(2) 

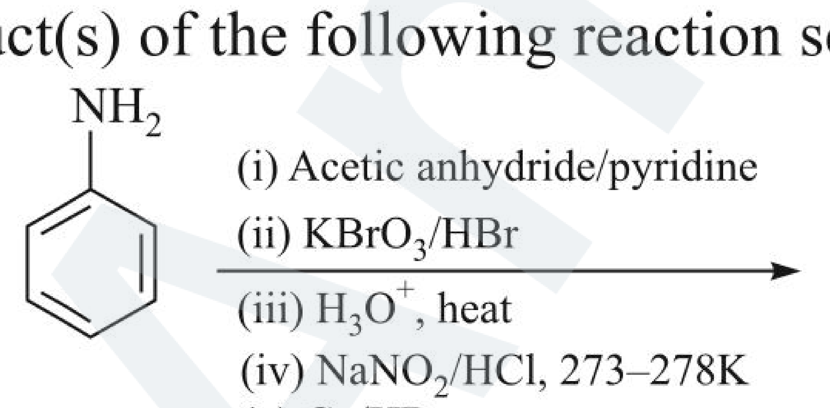
(3) 

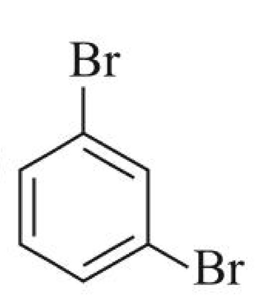
(4) 

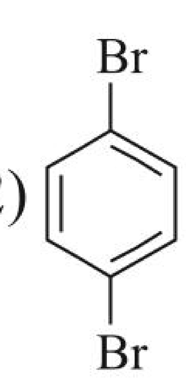
(JEE Advanced 2018)

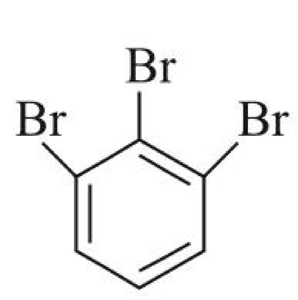
Multiple Correct Answers Type

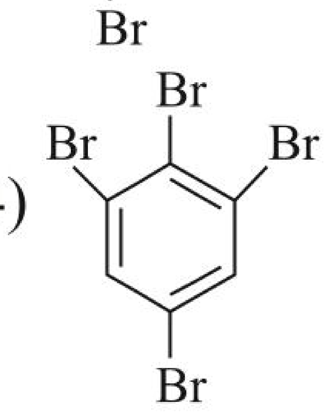
1. The product(s) of the following reaction sequence is(are)



(1) 

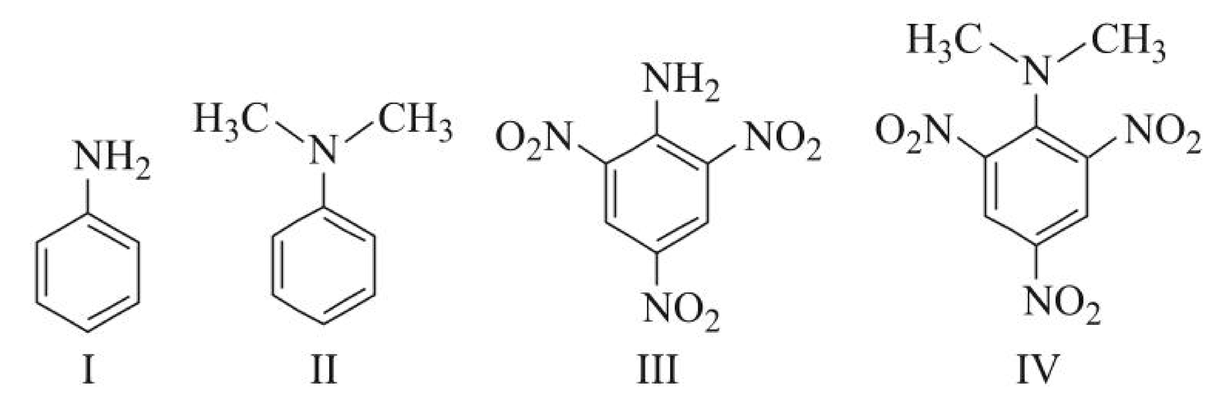
(2) 

(3) 

(4) 

(JEE Advanced 2016)

2. Consider the following four compounds I, II, III, and IV.



Choose the correct statement(s).

(1) The order of basicity is II > I > III > IV.

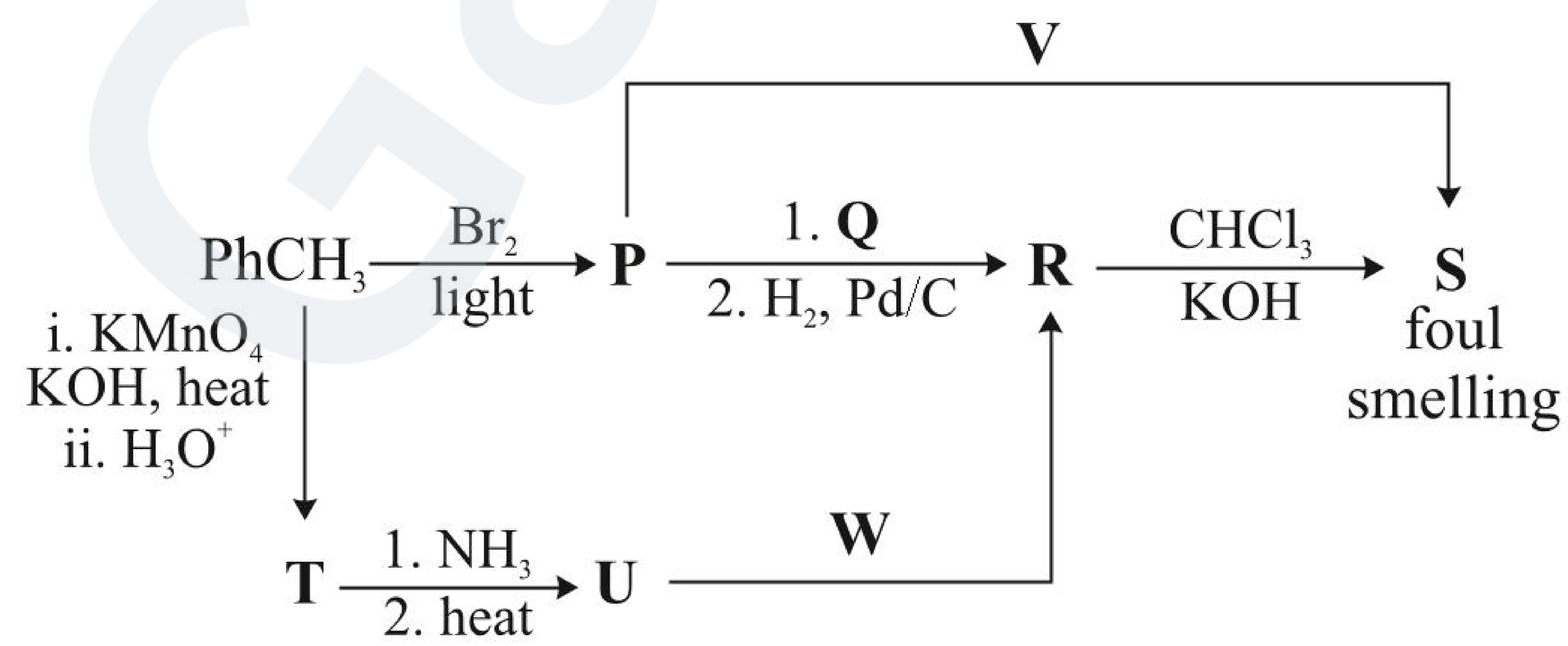
(2) The magnitude of pK_b difference between I and II is more than that between III and IV.

(3) Resonance effect is more in III than in IV.

(4) Steric effect makes compound IV more basic than III.

(JEE Advanced 2020)

3. Correct option(s) for the following sequence of reactions is(are)



(1) Q = KNO_2, W = $LiAlH_4$

(2) R = benzenamine, V = KCN

(3) Q = $AgNO_2$, R = phenylmethanamine

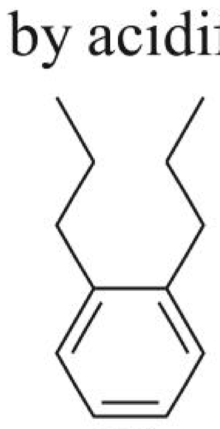
(4) W = $LiAlH_4$, V = AgCN

(JEE Advanced 2021)

Linked Comprehension Type

Paragraph 1

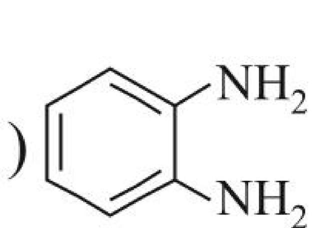
Treatment of compound *O* with $KMnO_4/H^+$ gave *P*, which on heating with ammonia gave *Q*. The compound *Q* on treatment with Br_2/NaOH produced *R*. On strong heating, *Q* gave *S*, which on further treatment with ethyl 2-bromopropanoate in the presence of KOH followed by acidification, gave a compound *T*.

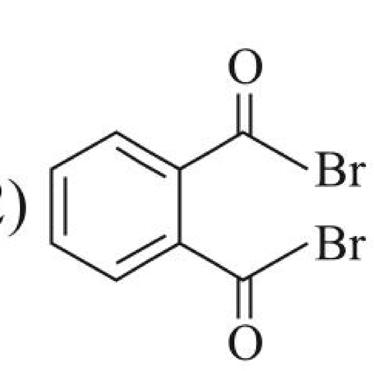


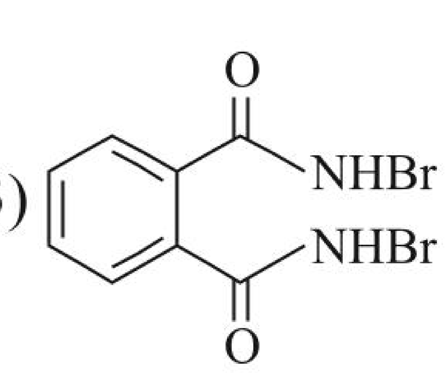
(O)

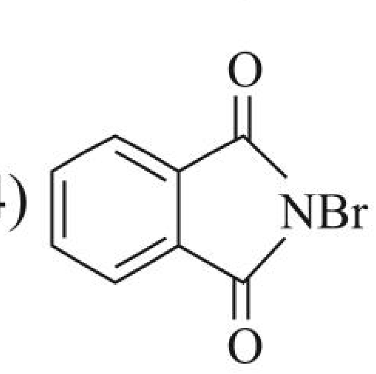
(JEE Advanced 2016)

1. The compound *R* is

(1) 

(2) 

(3) 

(4) 

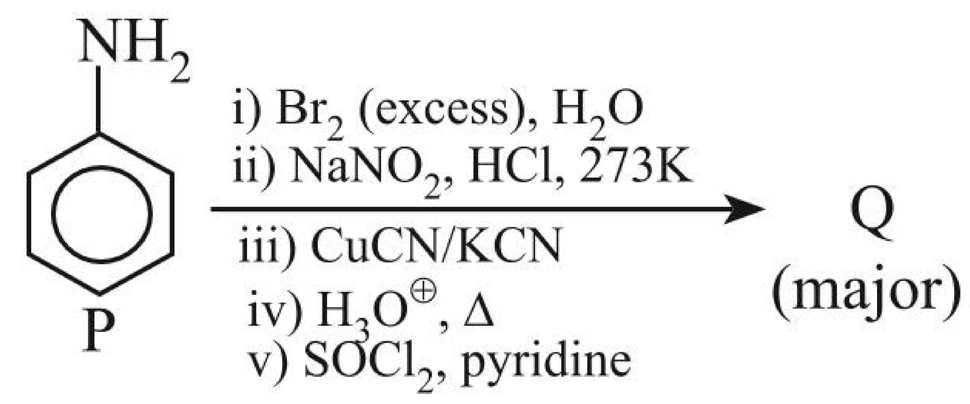
2. The compound T is

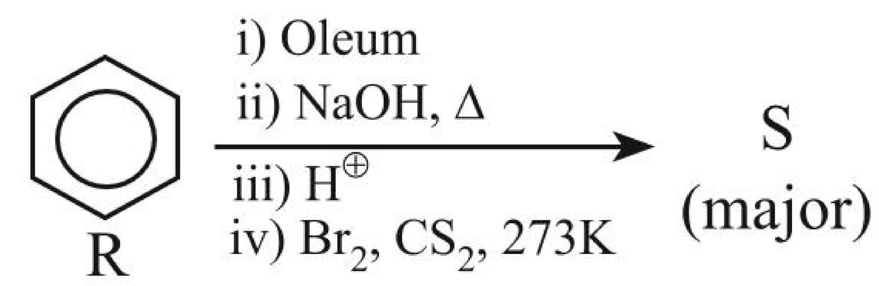
(1) glycine (2) alanine

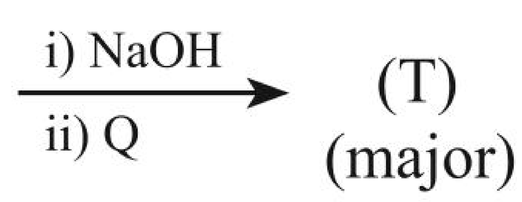
(3) valine (4) serine

Numerical Value Type

1. Schemes 1 and 2 describe the conversion of P to Q and R to S, respectively. Scheme 3 describes the synthesis of T from Q and S. The total number of Br atoms in a moleclue of T is

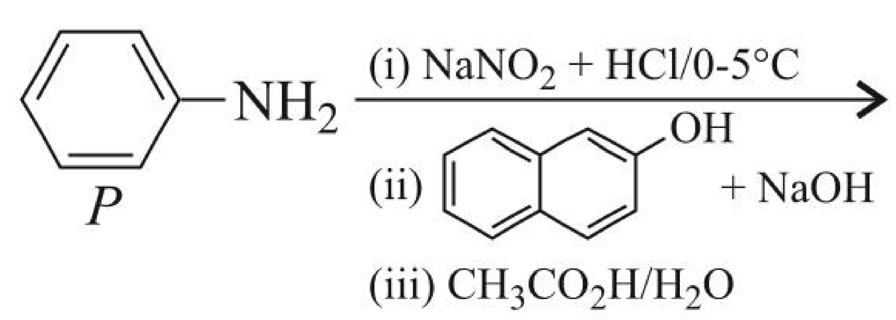
Scheme 1: 

Scheme 2 : 

Scheme 3 : 

(JEE Advanced 2019)

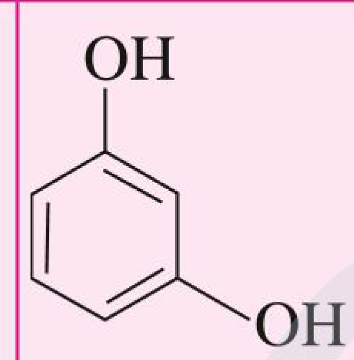
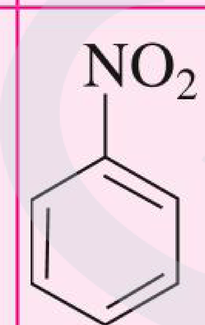
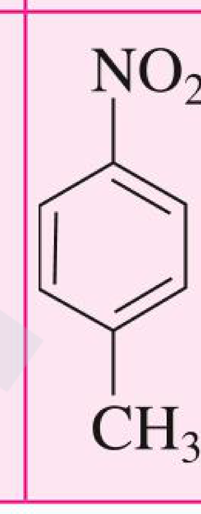
2. Consider the reaction sequence from P to Q shown below. The overall yield of the major product Q from P is 75%. What is the amount in grams of Q obtained from 9.3 mL of P? (Use density of P = 1.00 g mL^{-1}, Molar mass of C = 12.0, H = 1.0, O = 16.0 and N = 14.0 g mol^{-1})



(JEE Advanced 2020)

Matrix Match Type

1. Match the four starting materials **(P, Q, R, S)** given in List I with the corresponding reaction schemes **(I, II, III, IV)** provided in List II and select the correct answer using the code given below the lists.

	List I		List II
P.	H—≡—H	1.	**Scheme I** (i) $KMnO_4$, $\overset{\ominus}{H O}$, heat (ii) $H^{\oplus}$, H_2O (iii) $SOCl_2$ (iv) NH_3 ? $\longrightarrow C_7H_6N_2O_3$
Q.		2.	**Scheme II** (i) Sn/HCl (ii) CH_3COCl (iii) conc. H_2SO_4 (iv) HNO_3 (v) dil. H_2SO_4, heat (vi) $\overset{\ominus}{H O}$? $\longrightarrow C_6H_6N_2O_2$
R.		3.	**Scheme III** (i) red hot iron, 873 K (ii) fuming HNO_3, H_2SO_4, heat (iii) $H_2S.NH_3$ (iv) $NaNO_2$, H_2SO_4 (v) hydrolysis ? $\longrightarrow C_6H_5NO_3$
S.		4.	**Scheme IV** (i) conc. H_2SO_4, 60°C (ii) conc. HNO_3, conc. H_2SO_4 (iii) dil. H_2SO_4, heat ? $\longrightarrow C_6H_5NO_4$

Code:

	P	Q	R	S
(1)	1	4	2	3
(2)	3	1	4	2
(3)	3	4	2	1
(4)	4	1	3	2

(JEE Advanced 2014)

Answers Key

EXERCISES

1. (4)	**2.** (3)	**3.** (3)	**4.** (3)	**5.** (1)
6. (4)	**7.** (3)	**8.** (4)	**9.** (1)	**10.** (3)
11. (1)	**12.** (1)	**13.** (3)	**14.** (2)	**15.** (3)
16. (1)	**17.** (1)	**18.** (2)	**19.** (3)	**20.** (1)
21. (2)	**22.** (3)	**23.** (2)	**24.** (4)	**25.** (3)
26. (1)	**27.** (2)	**28.** (2)	**29.** (3)	**30.** (2)
31. (2)	**32.** (2)	**33.** (4)	**34.** (3)	**35.** (4)
36. (4)	**37.** (2)	**38.** (4)	**39.** (3)	**40.** (1)
41. (4)	**42.** (4)	**43.** (2)	**44.** (1)	**45.** (3)
46. (3)	**47.** (2)	**48.** (4)	**49.** (1)	**50.** (1)
51. (3)	**52.** (4)	**53.** (3)	**54.** (2)	**55.** (2)
56. (3)	**57.** (1)	**58.** (4)	**59.** (2)	**60.** (2)
61. (3)	**62.** (2)	**63.** (2)	**64.** (2)	**65.** (2)
66. (1)	**67.** (3)	**68.** (2)	**69.** (1)	**70.** (2)
71. (2)	**72.** (4)	**73.** (3)	**74.** (3)	**75.** (2)
76. (3)	**77.** (3)	**78.** (3)	**79.** (3)	**80.** (3)
81. (2)	**82.** (2)	**83.** (3)	**84.** (2)	**85.** (4)
86. (1)	**87.** (1)	**88.** (4)	**89.** (3)	**90.** (2)
91. (3)	**92.** (3)	**93.** (3)	**94.** (4)	**95.** (2)
96. (3)	**97.** (3)	**98.** (1)	**99.** (1)	**100.** (3)
101. (1)	**102.** (1)	**103.** (2)	**104.** (1)	**105.** (1)
106. (2)	**107.** (4)	**108.** (4)	**109.** (3)	**110.** (2)
111. (3)	**112.** (4)	**113.** (2)	**114.** (2)	**115.** (3)
116. (2)	**117.** (3)	**118.** (3)	**119.** (4)	**120.** (1)
121. (4)	**122.** (3)	**123.** (4)	**124.** (4)	**125.** (2)
126. (4)	**127.** (3)	**128.** (3)	**129.** (4)	**130.** (2)
131. (3)	**132.** (1)	**133.** (4)	**134.** (3)	**135.** (2)
136. (4)	**137.** (2)	**138.** (3)	**139.** (2)	**140.** (1)

Multiple Correct Answers Type

1. (1, 2, 3)	**2.** (1, 2, 3)	**3.** (1, 3, 4)
4. (3, 4)	**5.** (1, 2, 3)	**6.** (1, 3, 4)
7. (2, 4)	**8.** (2, 4)	**9.** (4)
10. (1, 2, 3, 4)	**11.** (2)	**12.** (1, 3, 4)
13. (1, 2, 4)	**14.** (1, 2, 3)	**15.** (1, 2, 3, 4)
16. (1, 2, 4)	**17.** (2, 4)	**18.** (2, 3, 4)
19. (2, 3, 4)	**20.** (2, 3, 4)	**21.** (2, 4)
22. (1, 2, 4)	**23.** (1, 2, 3, 4)	**24.** (2, 3)
25. (1, 3, 4)	**26.** (1, 3)	**27.** (1, 4)
28. (2, 4)	**29.** (1, 2, 3)	**30.** (1, 2, 3, 4)
31. (1, 2, 3)	**32.** (1, 2)	**33.** (1, 3, 4)
34. (1, 2, 3, 4)	**35.** (1, 2, 3, 4)	**36.** (1, 2, 3)
37. (2, 3)	**38.** (2, 3, 4)	**39.** (1, 2, 3)
40. (1, 2, 3, 4)	**41.** (1, 4)	**42.** (1, 4)
43. (1, 2, 4)	**44.** (1, 2)	**45.** (3, 4)
46. (1, 2, 3, 4)		

Linked Comprehension Type

1. (1)	**2.** (2)	**3.** (2)	**4.** (3)	**5.** (2)
6. (1)	**7.** (3)	**8.** (1)	**9.** (1)	**10.** (2)
11. (2)	**12.** (1)	**13.** (2)	**14.** (2)	**15.** (1)
16. (1)	**17.** (3)	**18.** (2)		

Matrix Match Type

S.No.	a	b	c	d	e	f
1	q, r	p	s	t	—	—
2	r	s	p	q	u	t
3	ii, p, r	i, q, s	ii, iii, t	iv, t	—	—

Numerical Value Type

1. (3)	**2.** (2)	**3.** (4)	**4.** (2)	**5.** (2)
6. (4)	**7.** (3)	**8.** (5)	**9.** (5)	

ARCHIVES

JEE Advanced

Single Correct Answer Type

1. (3)	**2.** (3)	**3.** (1)	**4.** (4)	**5.** (2)
6. (4)	**7.** (1)	**8.** (3)	**9.** (3)	**10.** (1)
11. (1)	**12.** (3)	**13.** (4)		

Multiple Correct Answers Type

1. (2) **2.** (3, 4) **3.** (3, 4)

Linked Comprehension Type

1. (1) **2.** (2)

Numerical Value Type

1. (4) **2.** (18.60)

Matrix Match Type

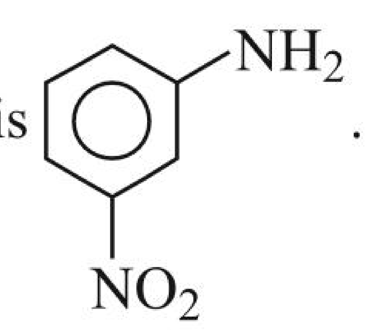
1. (3)

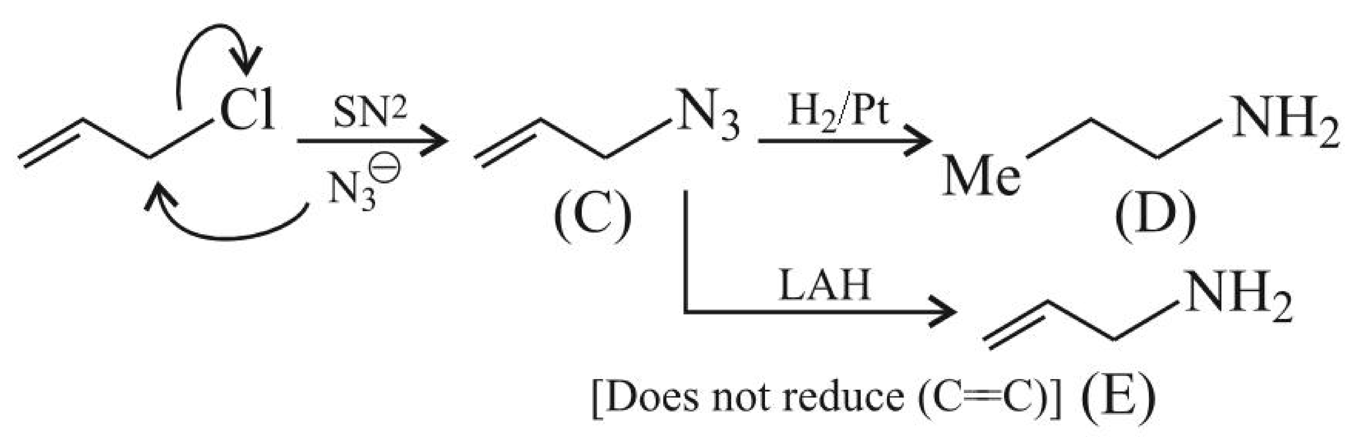
Chapter 7

Concept Application Exercises

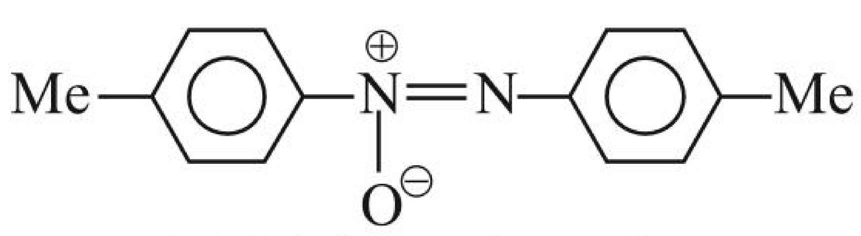
Exercise 7.1

1. i. $(NH_4)_2S$ or NH_4SH reduces only one nitro group.

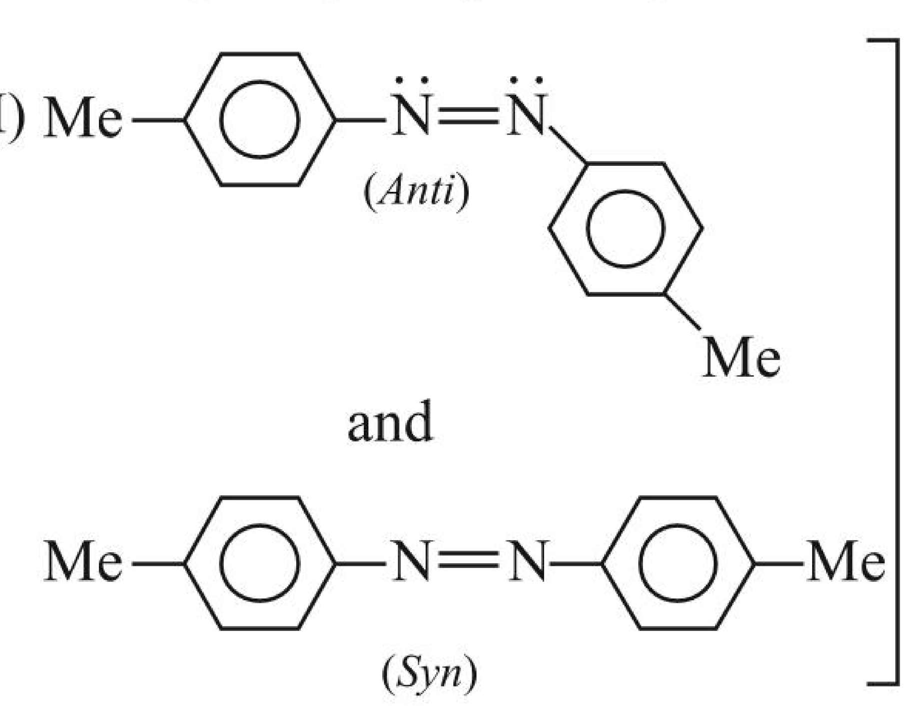
B is  .

ii. 

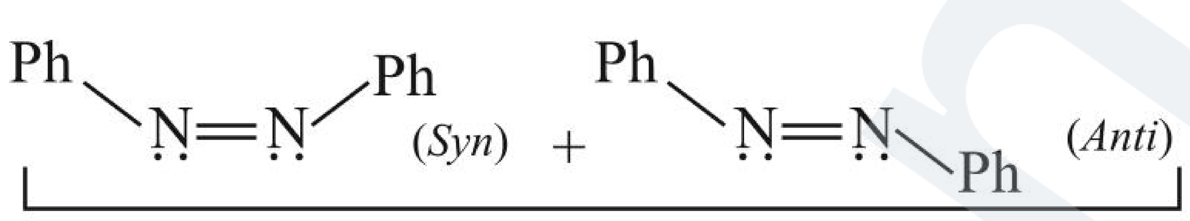
2. a. (I) PhNHOH (N-Phenyl hydroxylamine)

b. (II) 

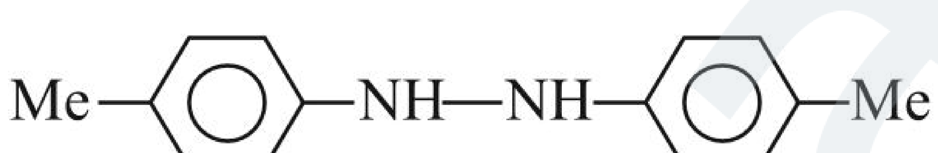
(*p*-Methyl azoxy benzene)

c. (III) 

p-Methyl azobenzene

d. (IV) 

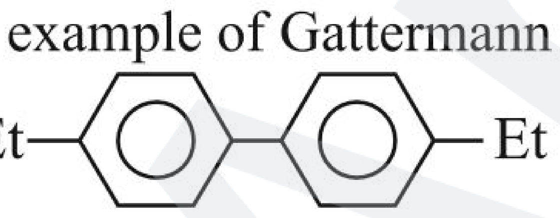
(Azo benzene)

e. (V) 

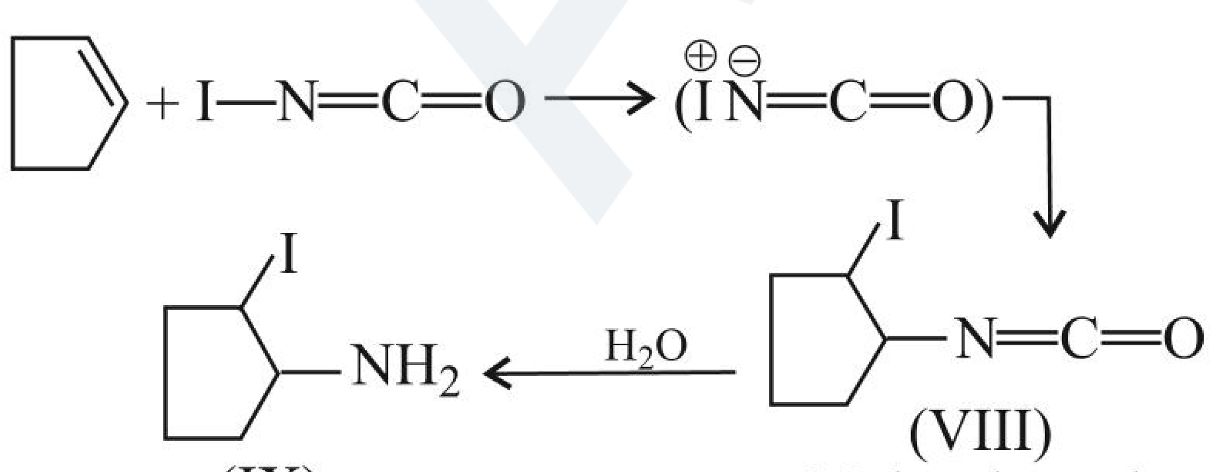
(*p*-Methyl hydrazobenzene)

f. (VI) $PhNHNH_2$ (Phenyl hydrazine)

g. It is an example of Gattermann reaction for making biphenyls.

(VII) 

(4,4′-Diethyl biphenyl)

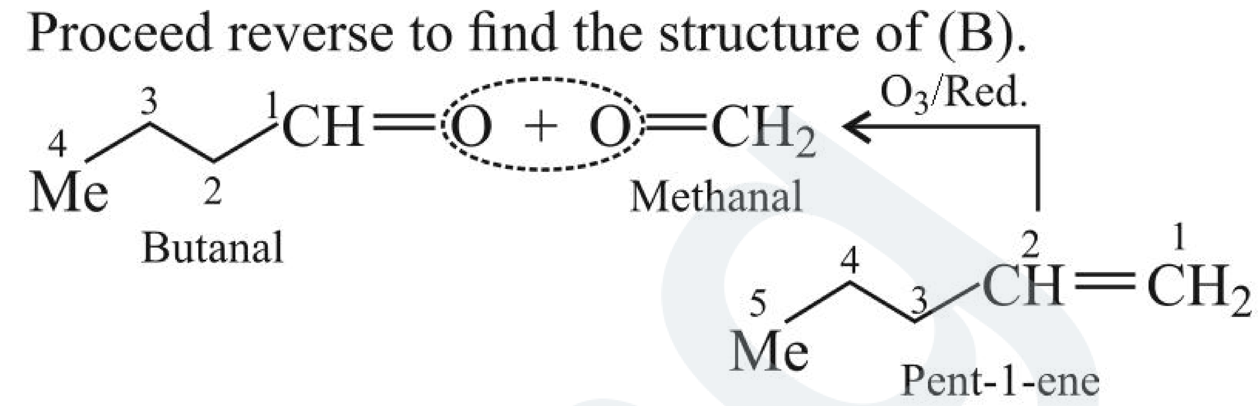
h. 

(IX) 2-Iodocyclopentyl amine

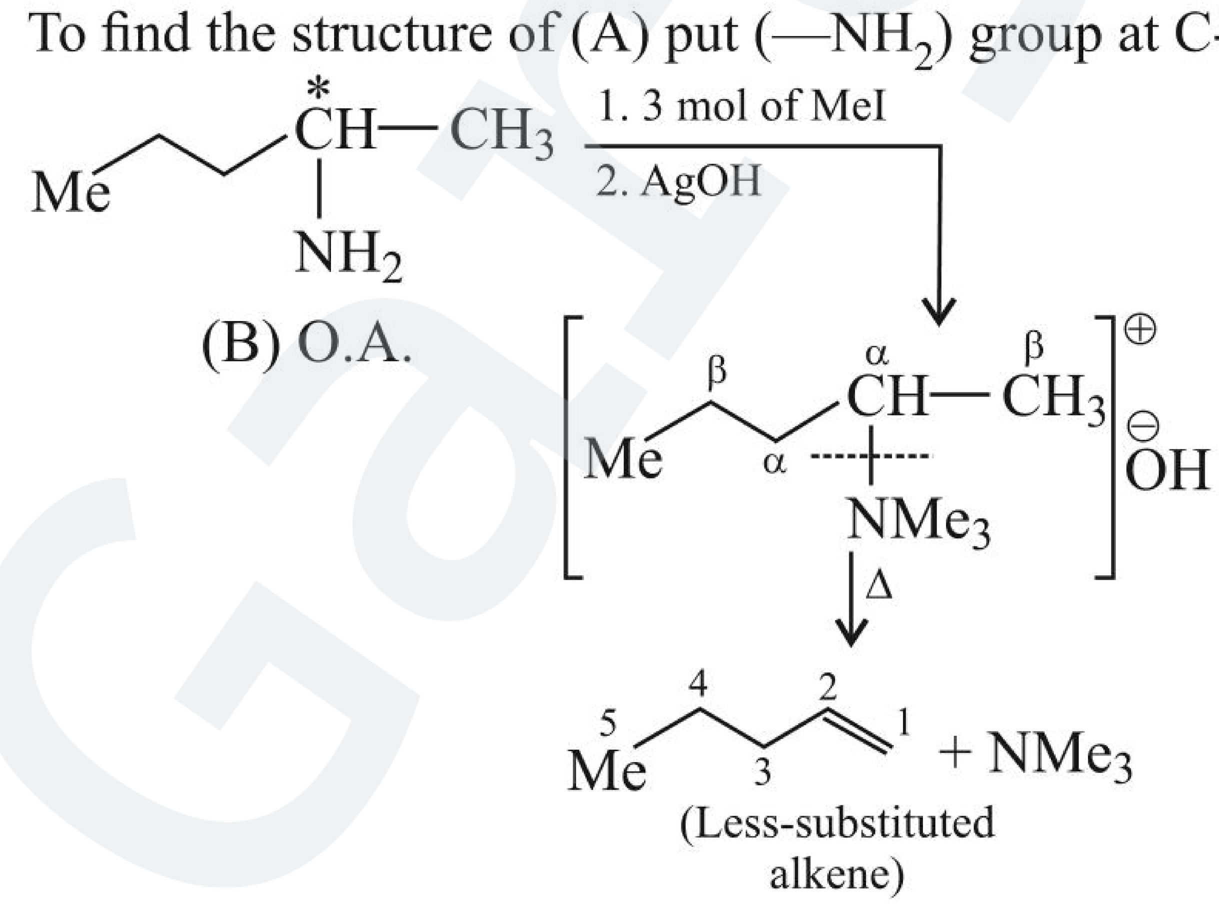
(VIII) 2-Iodocyclopentyl isocyanate

Exercise 7.2

1. Proceed reverse to find the structure of (B).



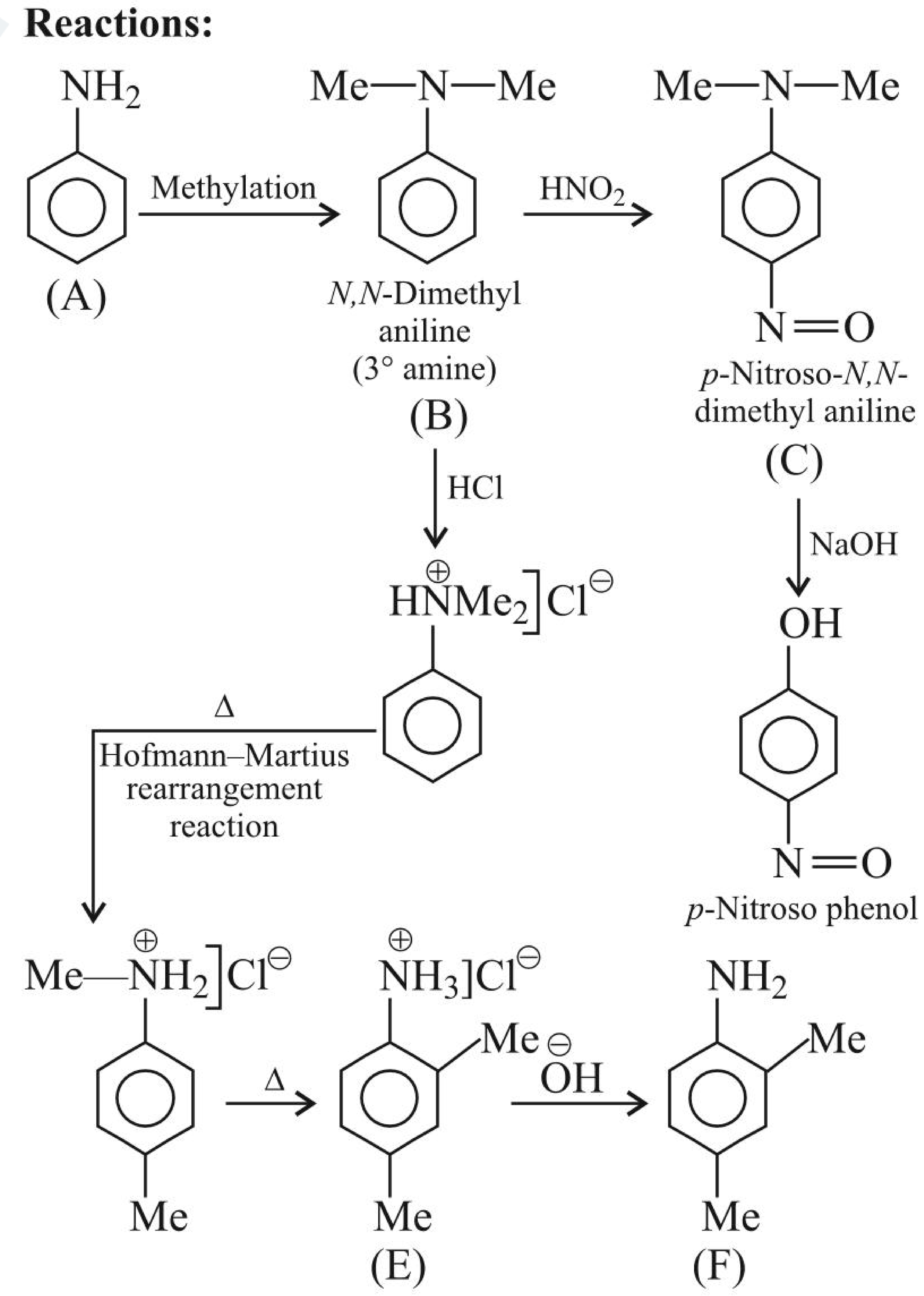
To find the structure of (A) put ($-NH_2$) group at C-2.



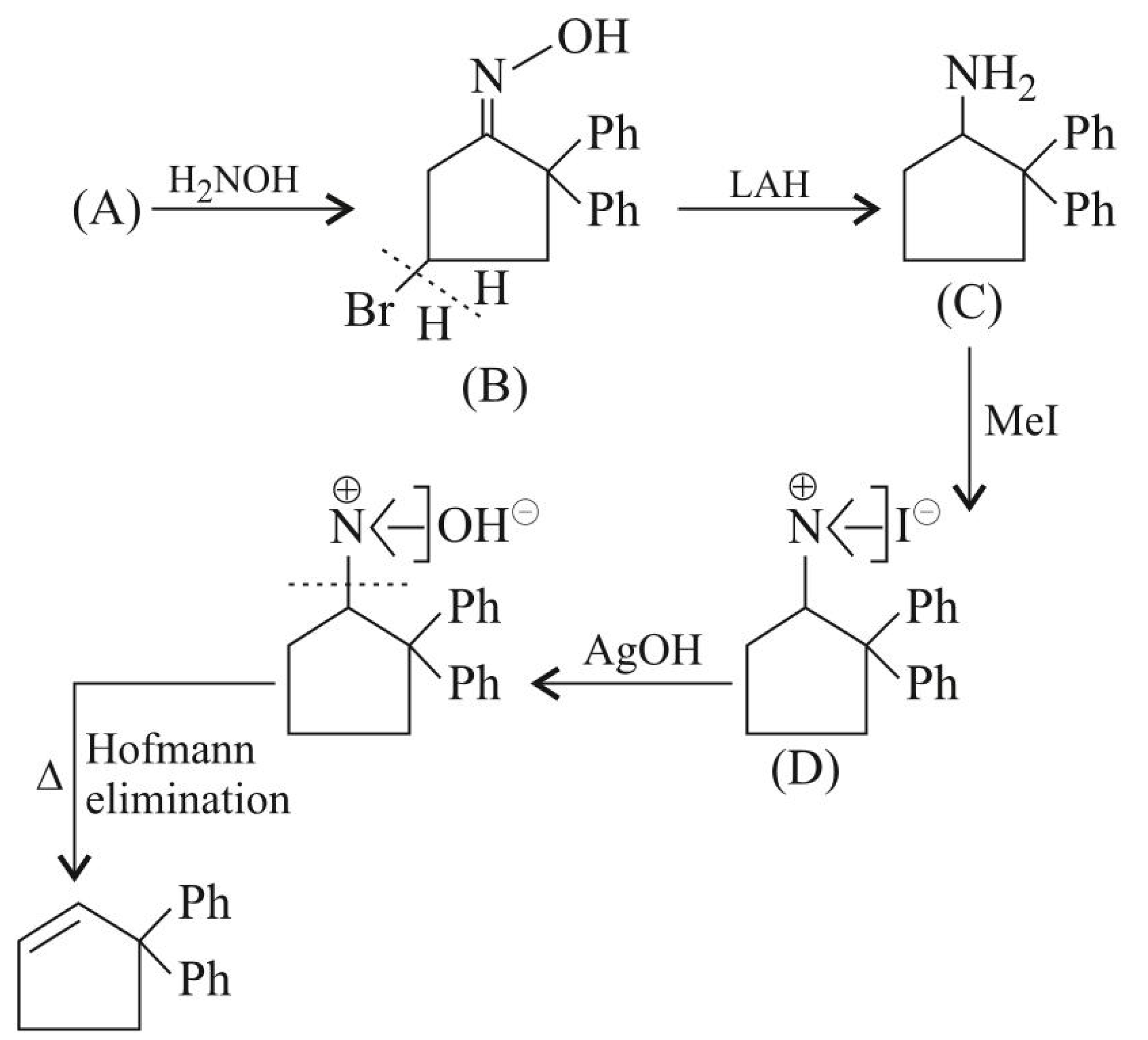
2. D.U. in A $= \dfrac{(2n_C + 2) - (n_H - n_N)}{2} = \dfrac{14 - (7-1)}{2} = 4°$

4 D.U. is A and C : H ≈ 1 : 1 suggest that (A) contains benzene ring. Therefore, (A) is aniline.

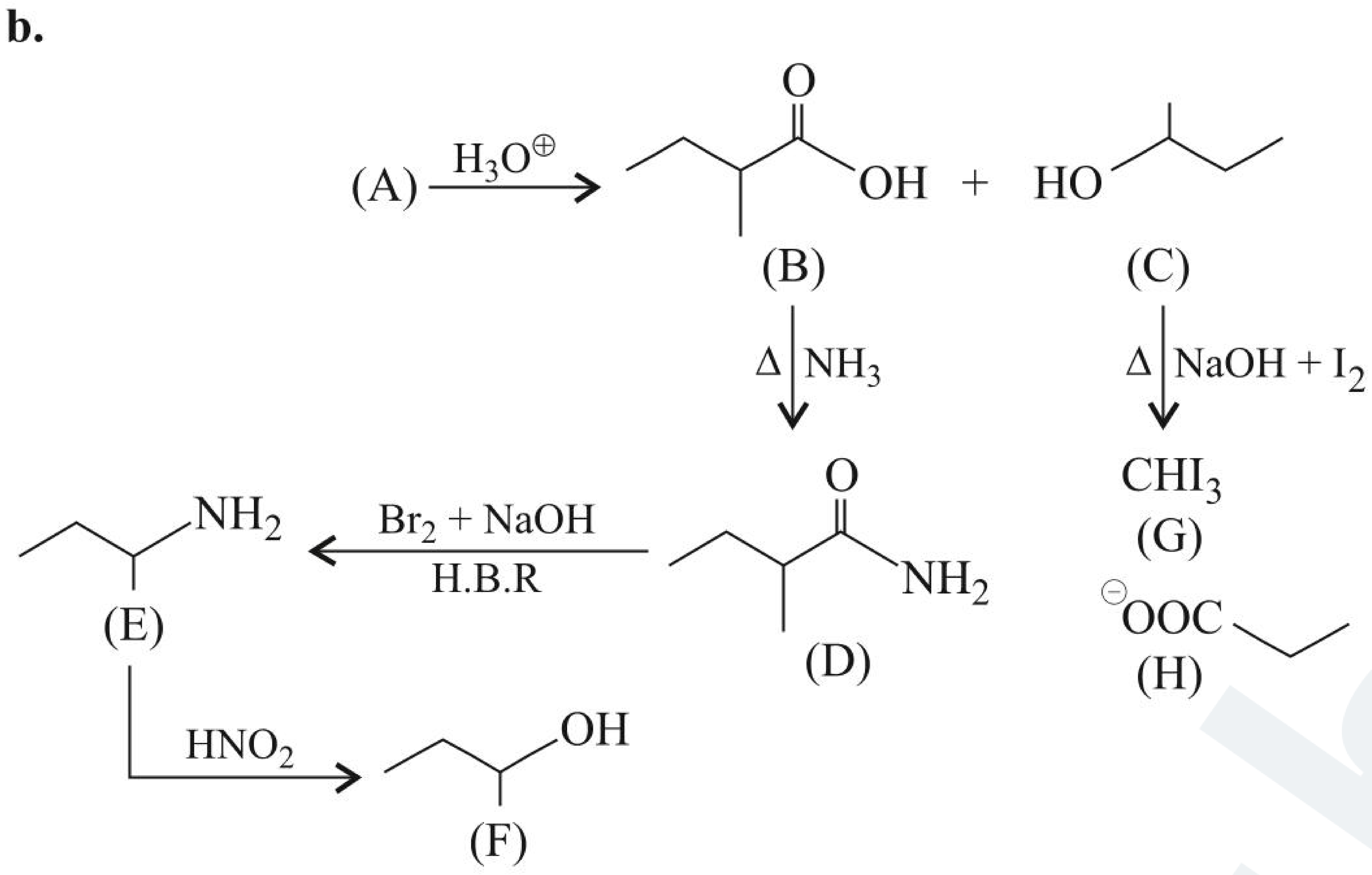
Reactions:



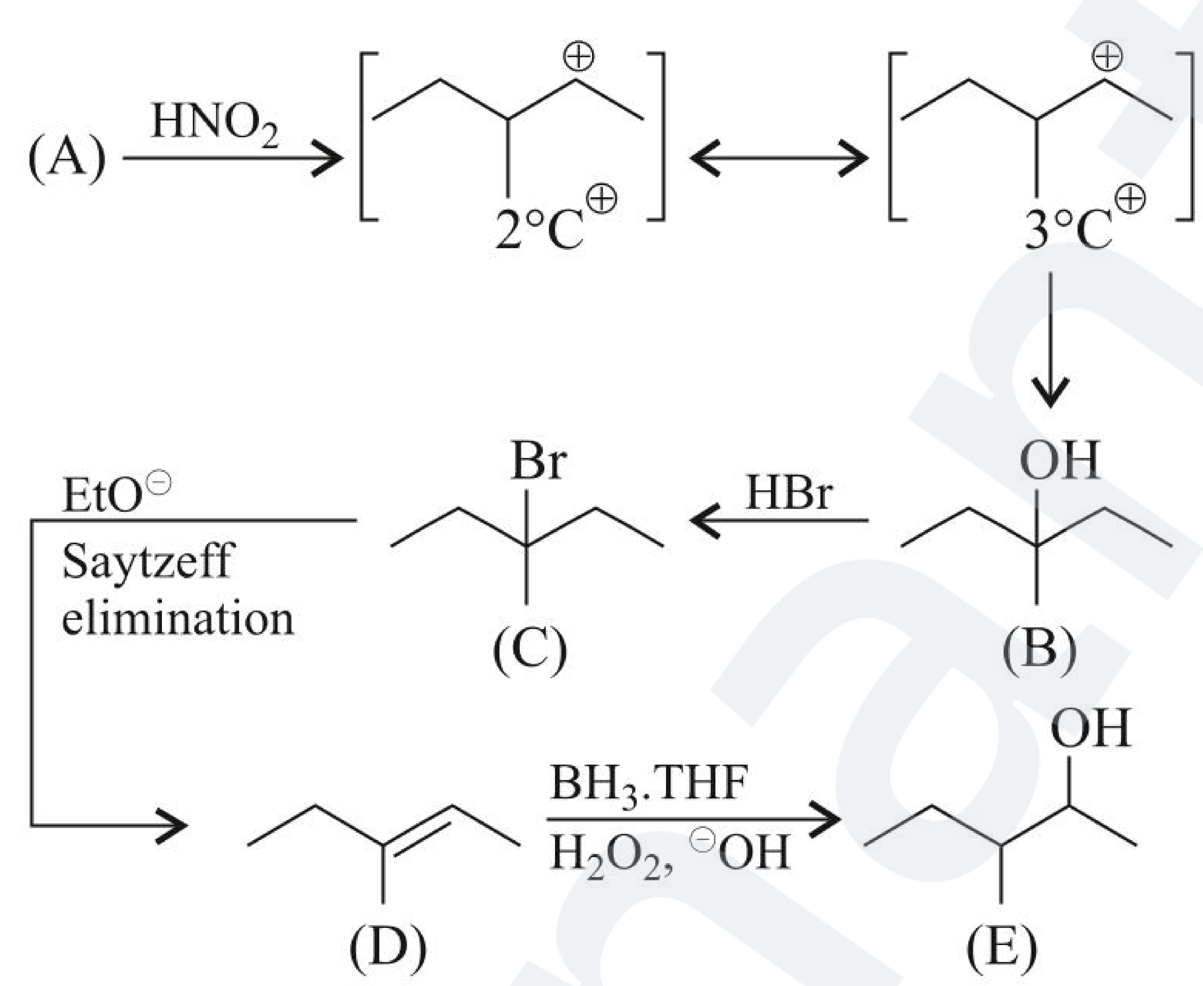
3. a.



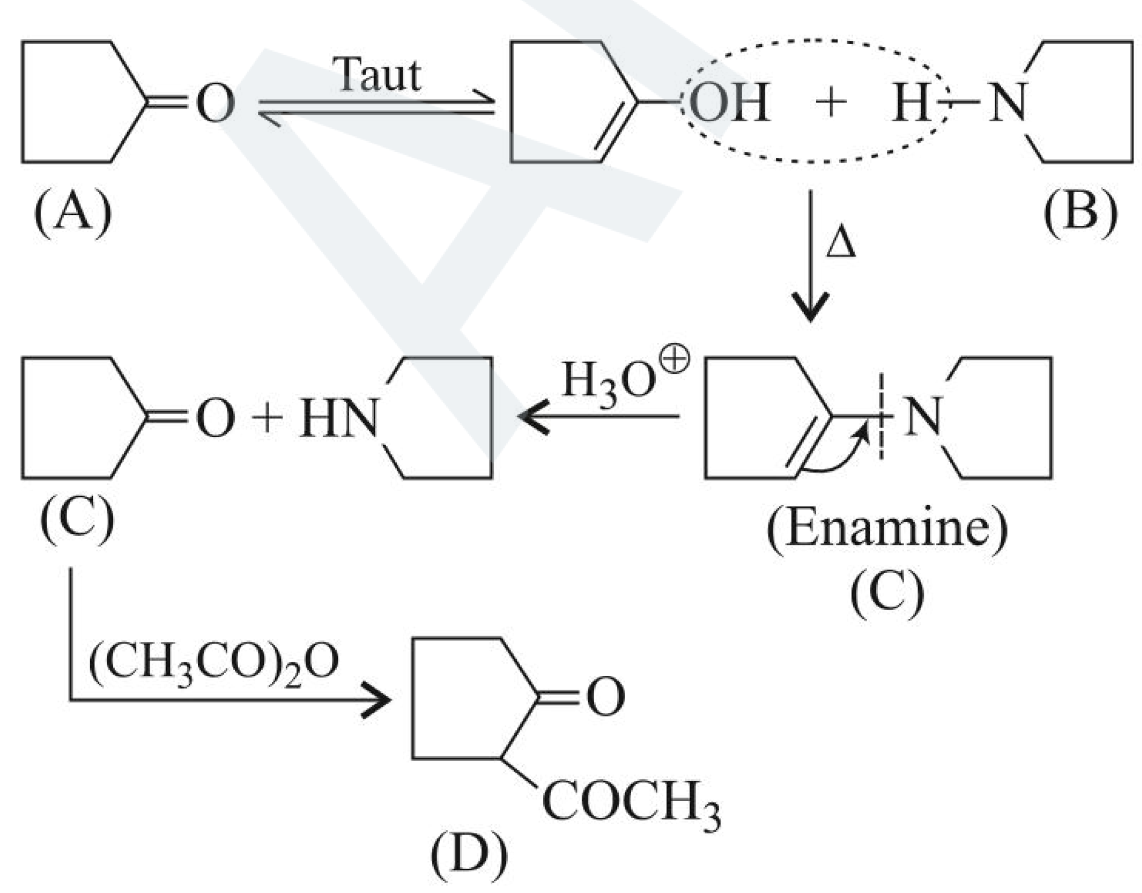
b.



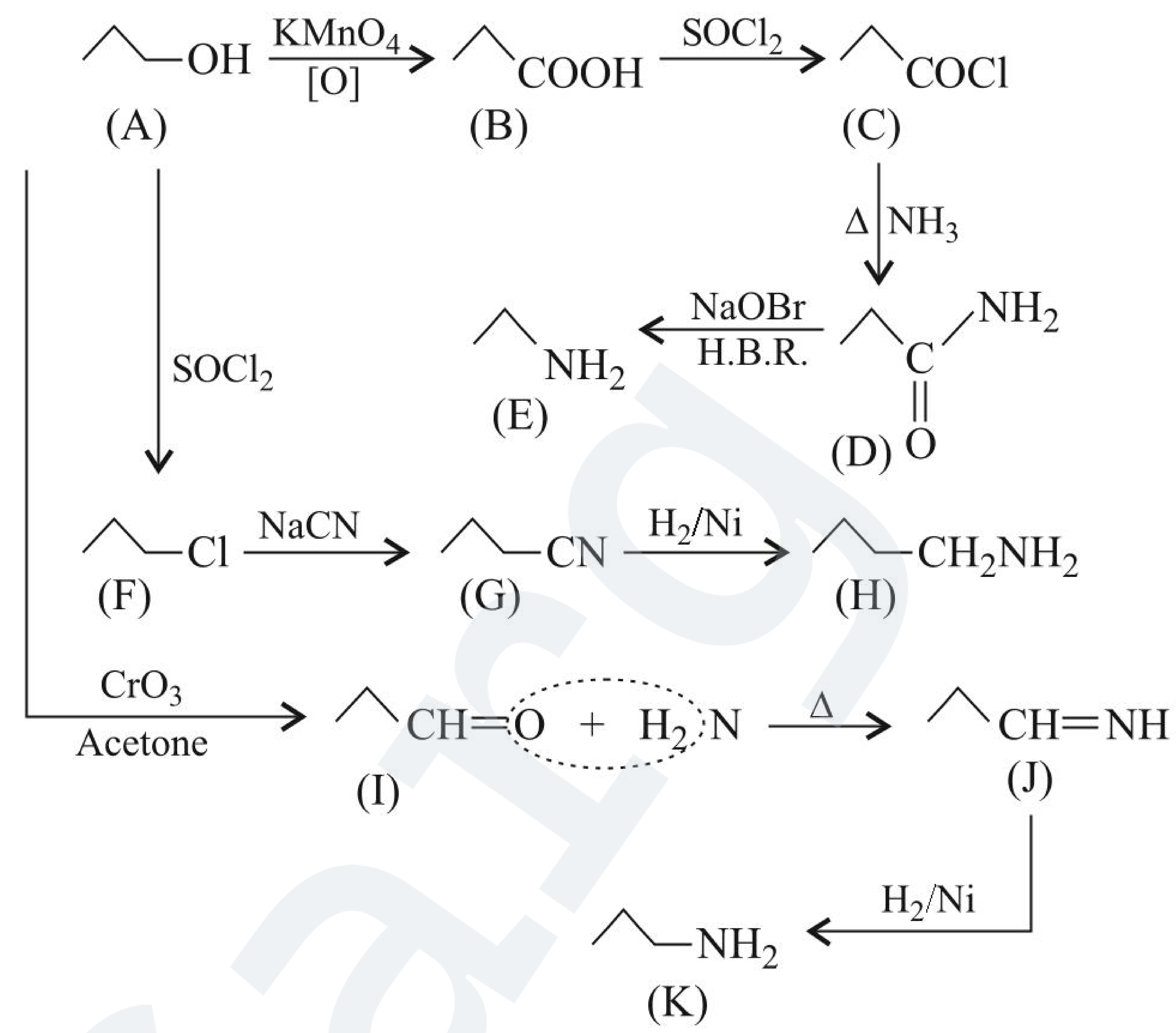
c.

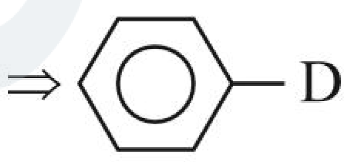


d.

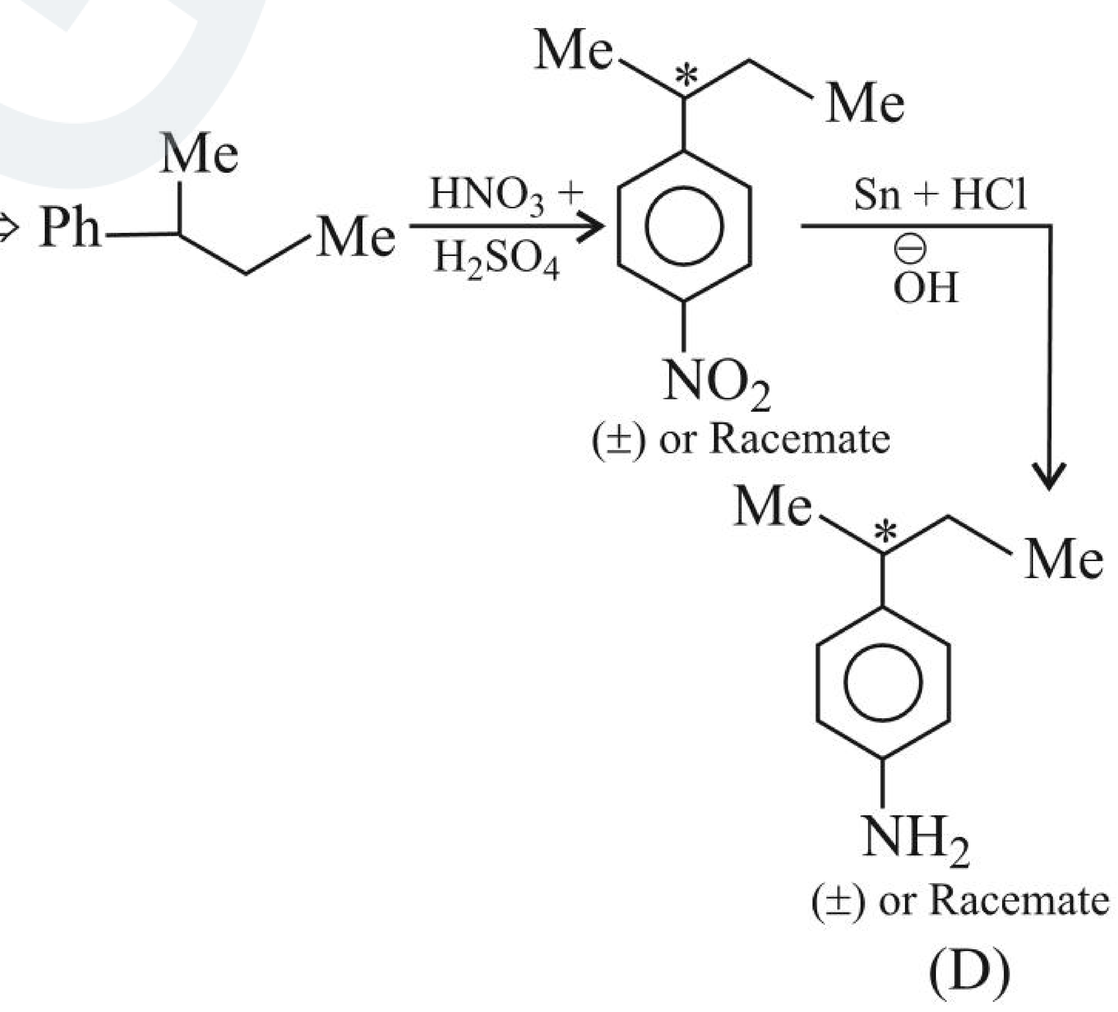


e.



4. a. (B) ⇒ $PhN_2^{\oplus}$ (C) ⇒  D

b. (C) ⇒

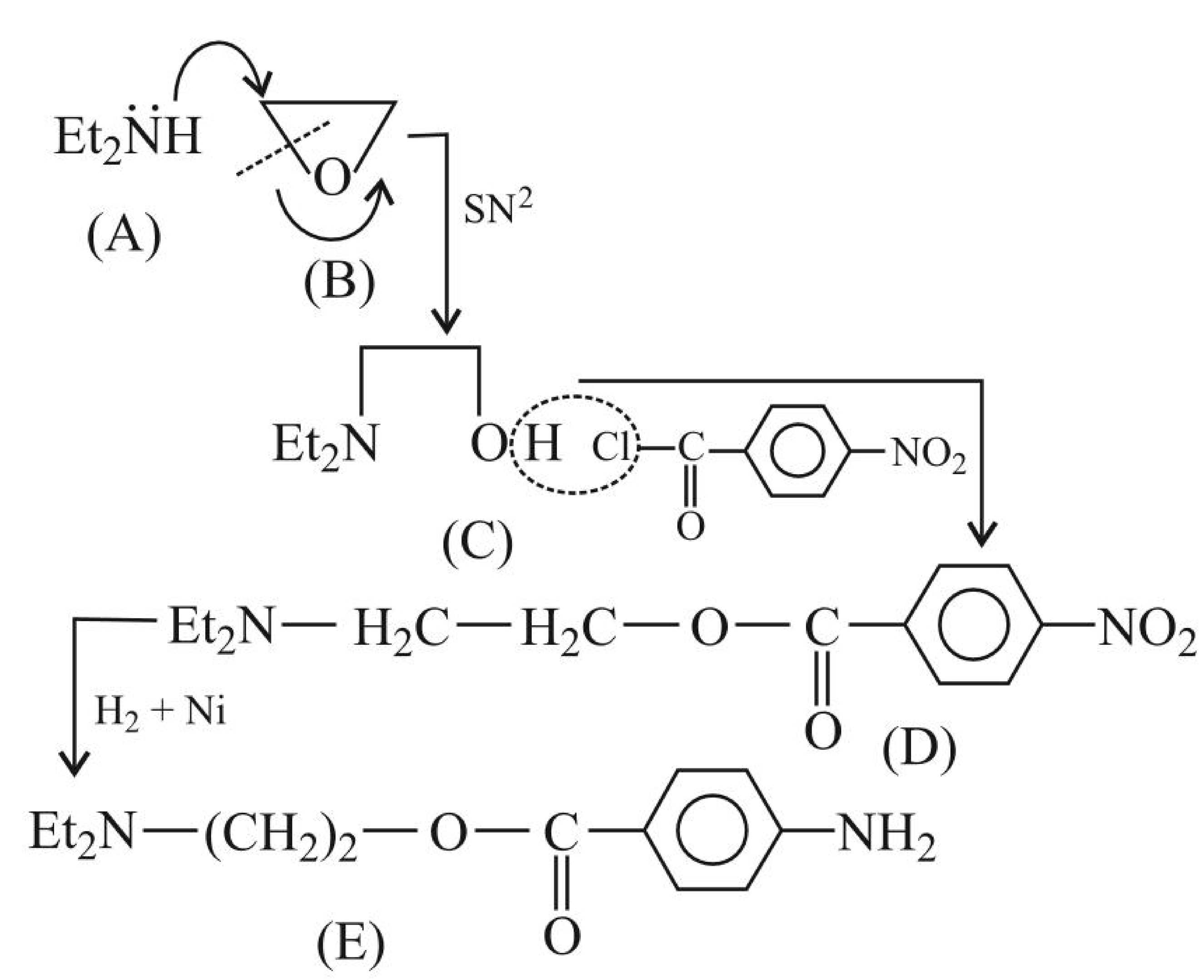


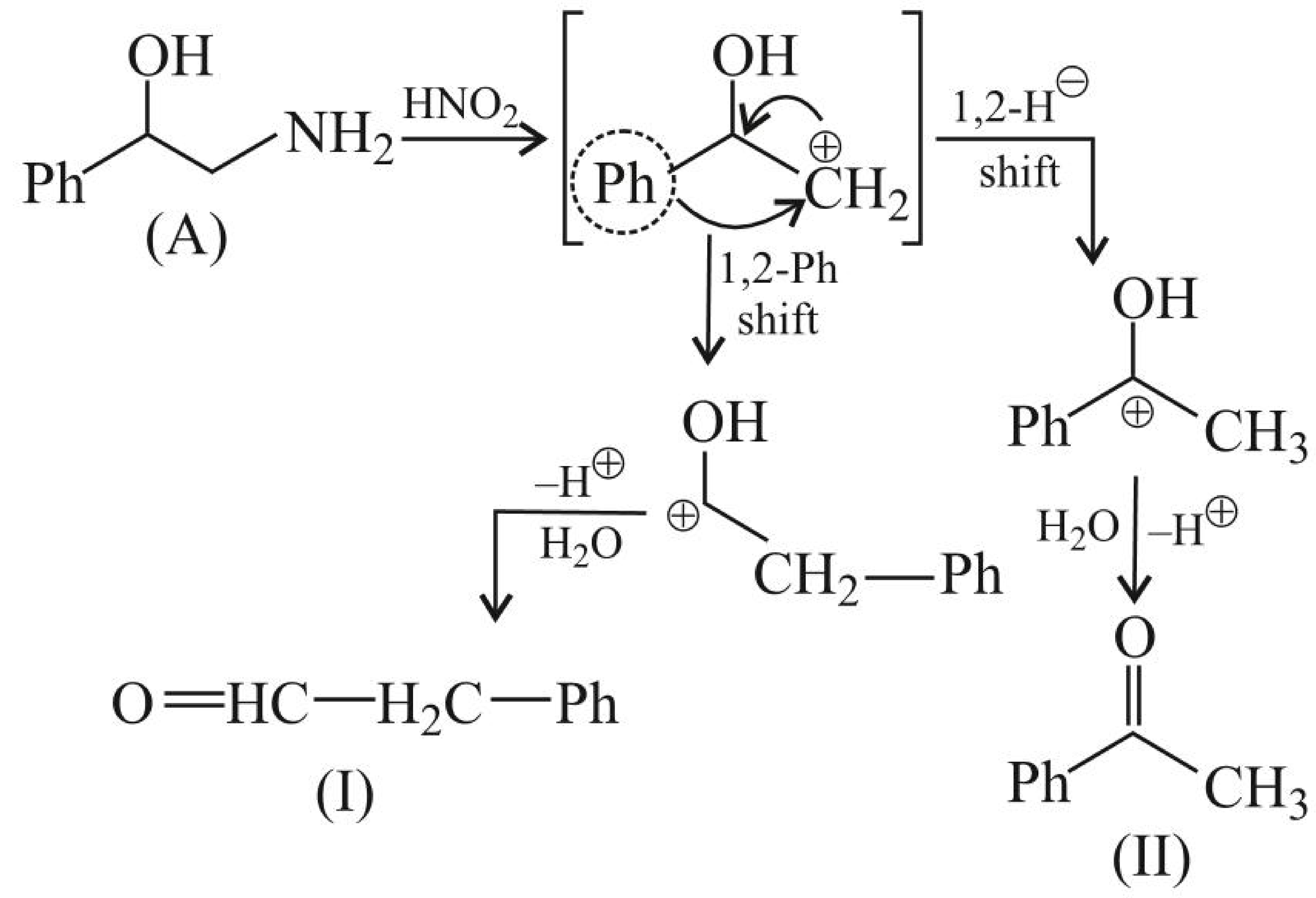
c. (C) ⇒ $Ph\underset{|}{C}H—CN$ (D) ⇒ $Ph—\underset{|}{C}H—CH_2NH_2$
OH OH

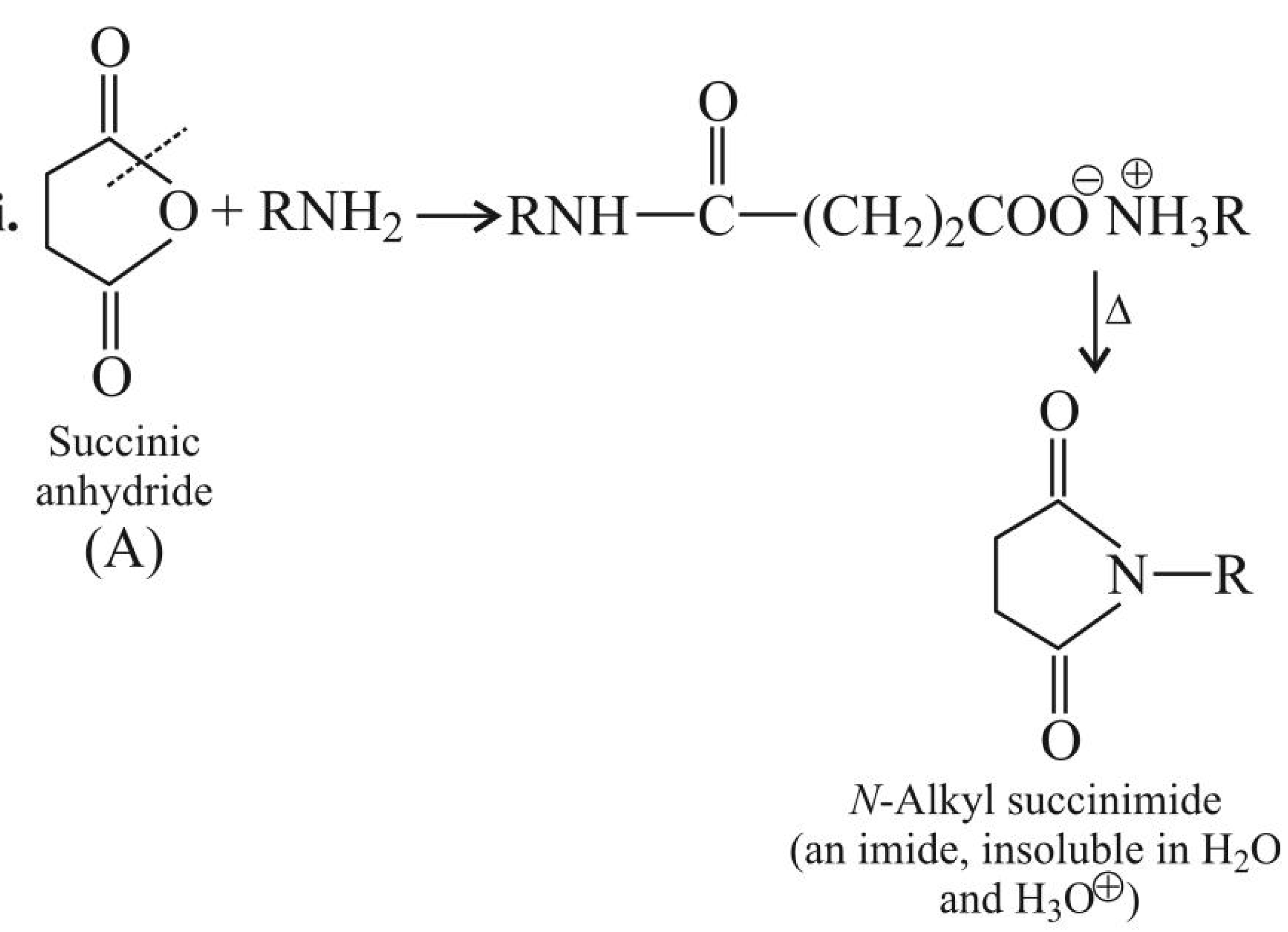
d. $PhCH{=}O + H_2\overset{\alpha}{C}H—NO_2 \xrightarrow[\text{Aldol type}]{\overset{\ominus}{O}H} PhCH{=}CH—NO_2$
(A) (B) (C)

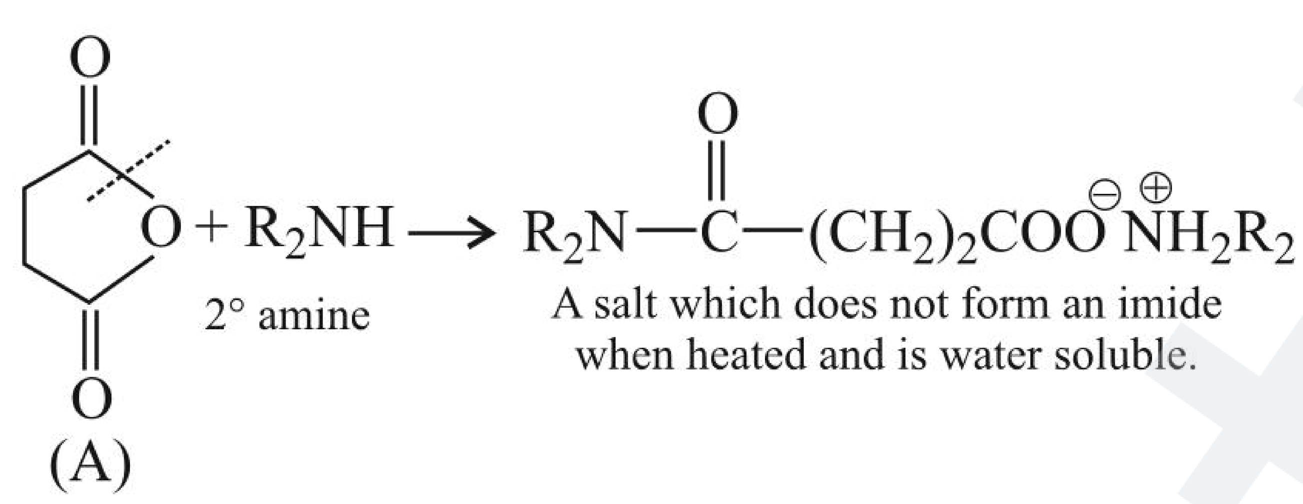
$PhCH{=}CH—NH_2 \xleftarrow[H^{\oplus}]{Fe^{2+}} PhCH{=}CH—NO_2$
(D) (C)

e.



5. 

6. a. i. 

ii. 

iii. 3° amine does not react with (A). The unreacted amine dissolves in aqueous acid ($H_3O^{\oplus}$).

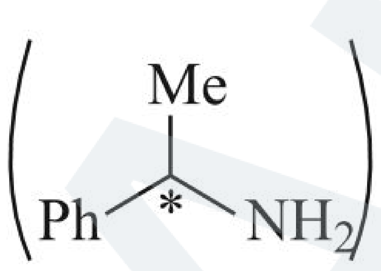
b. The amines must be water-insoluble liquids.

c. D.U. in (X) $= \dfrac{(2n_C + 2) - (n_H - n_N)}{2} = \dfrac{18 - 10}{2} = 4°$

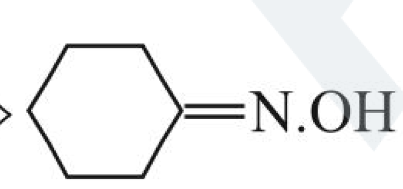
i. 4 D.U. in (X) suggests that it contains benzene ring.

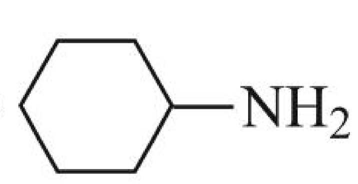
ii. (X) is a 1° amine since it dissolves in HCl and gives N_2 with HNO_2.

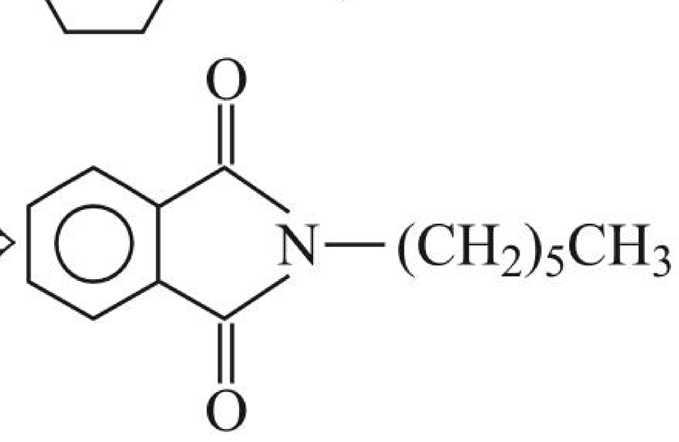
iii. The remaining C atom and the NH_2 must form a chiral molecule.

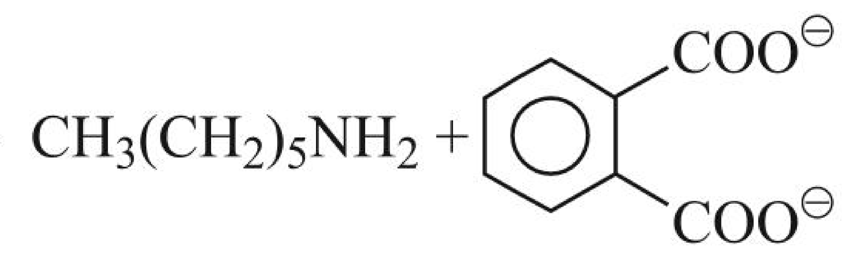
So, (X) is: 

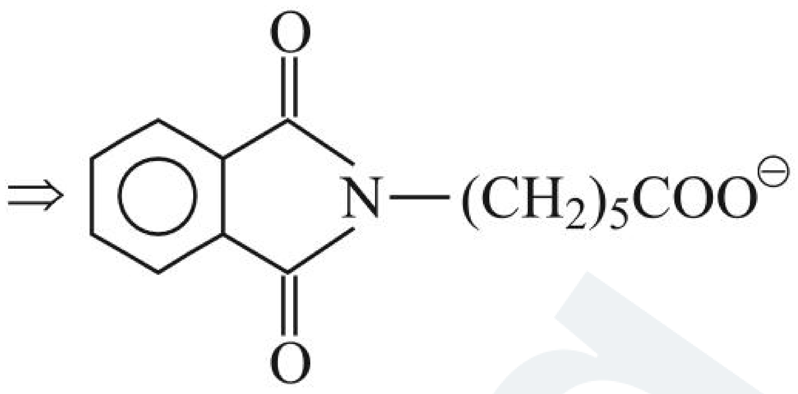
Exercise 7.3

1. a. (A) ⇒ 

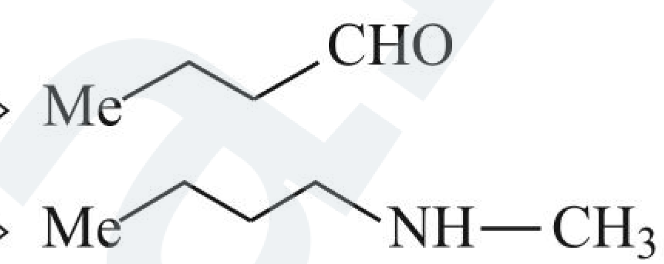
(B) ⇒ 

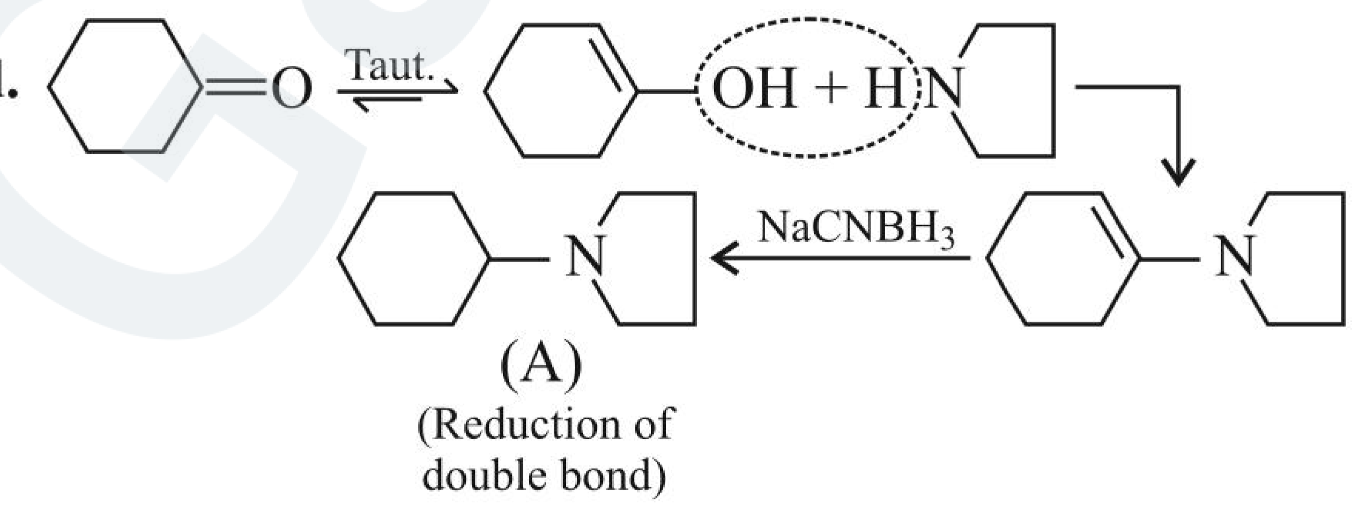
b. (A) ⇒ 

(B) ⇒ 

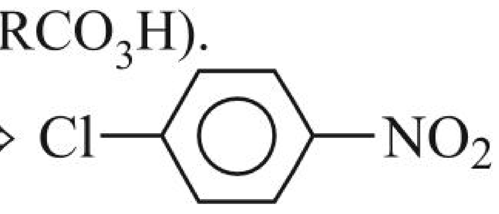
(C) ⇒ 

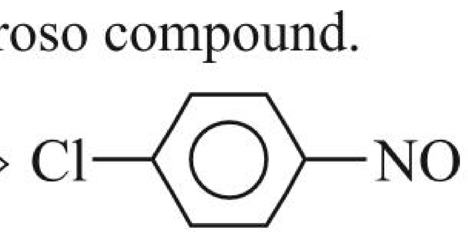
(D) ⇒ 

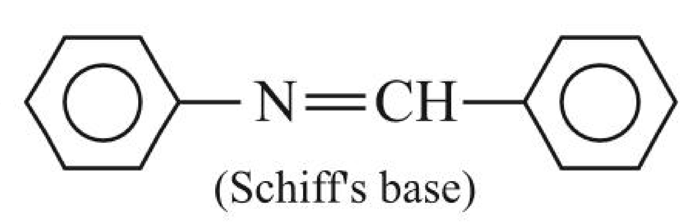
c. 

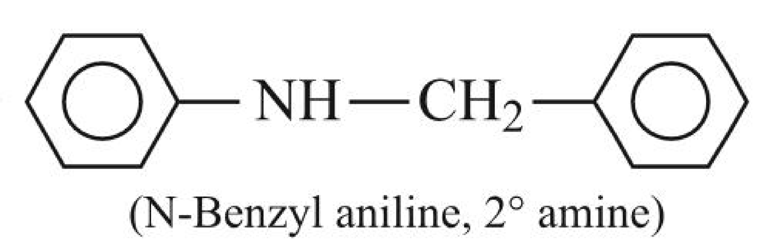
d. 

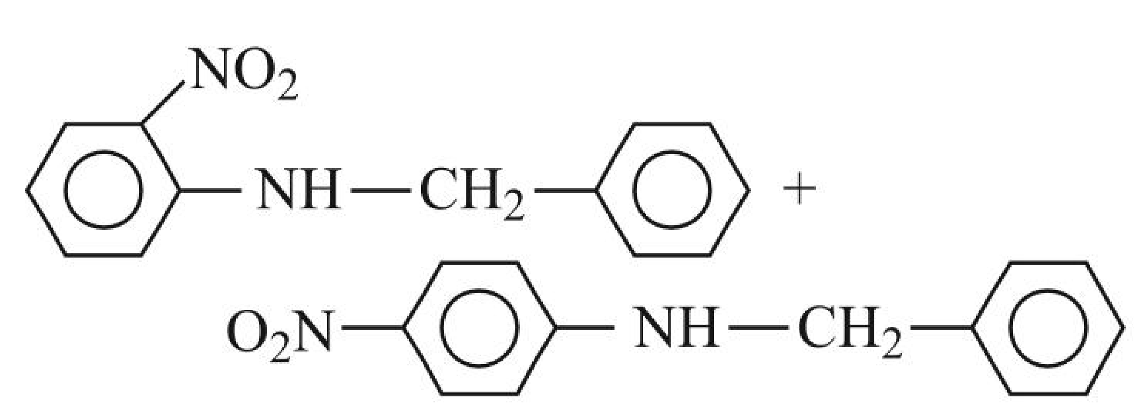
e. Amino compounds are oxidised to (—NO_2) compound by peracid (RCO_3H).

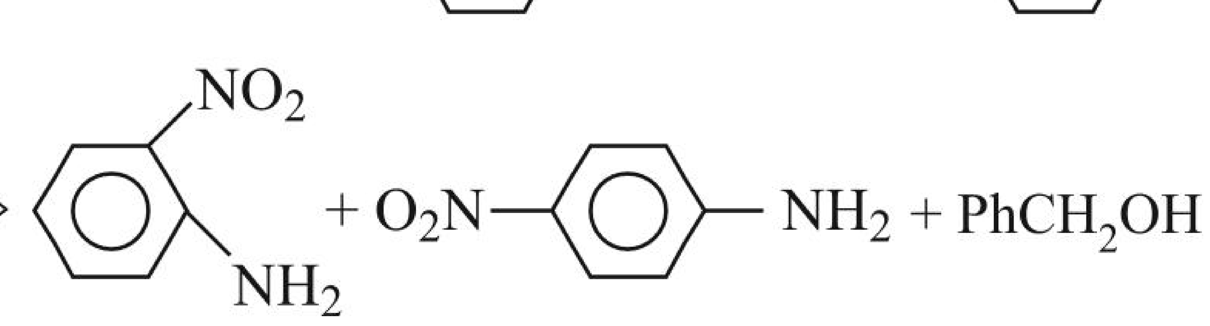
(A) ⇒  but with Caro's acid (H_2SO_5), it gives nitroso compound.

(B) ⇒ 

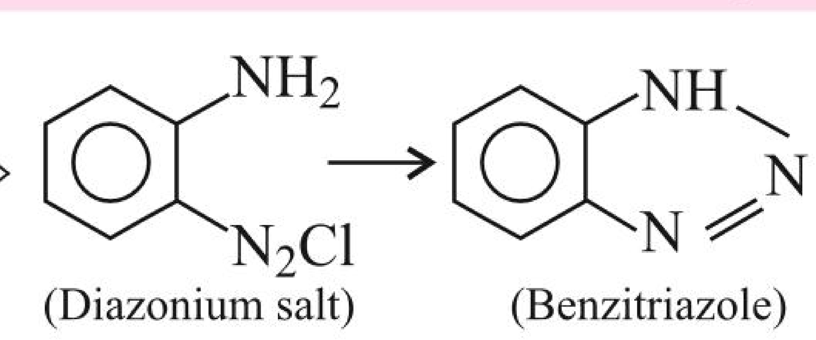
2. (A) ⇒ 

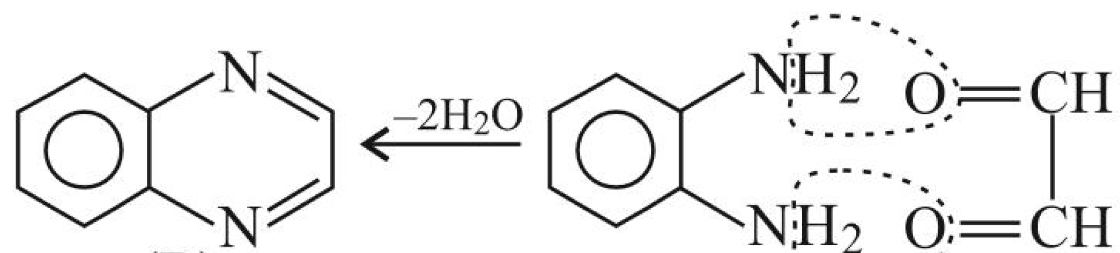
(B) ⇒ 

(C) ⇒ 

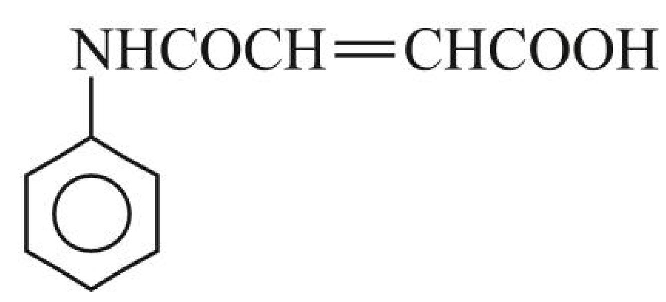
(D) ⇒ 

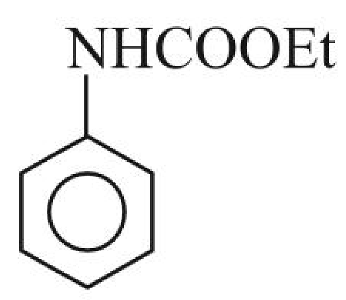
Note: NH_2 group is susceptible to oxidation when present in the ring. Hence before nitration is done, this can be protected by the formation of Schiff's base which can be hydrolysed to free base.

3. a. (A) ⇒ 

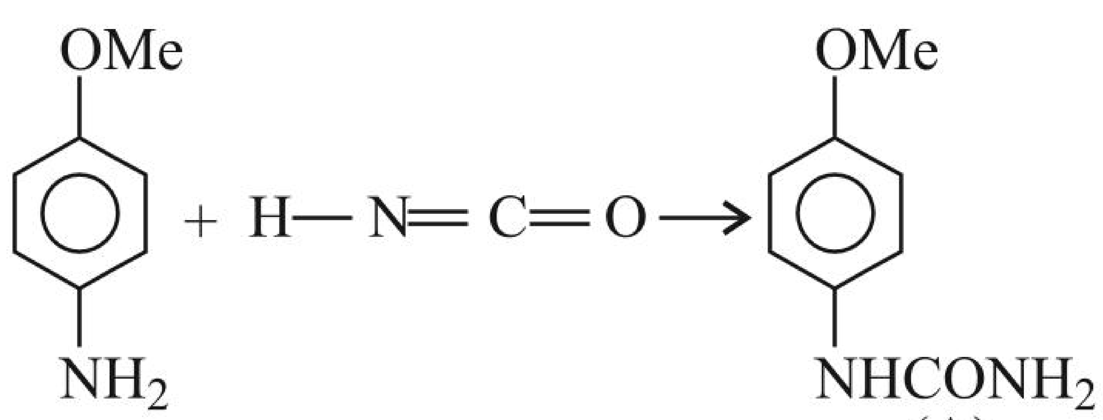


(B)

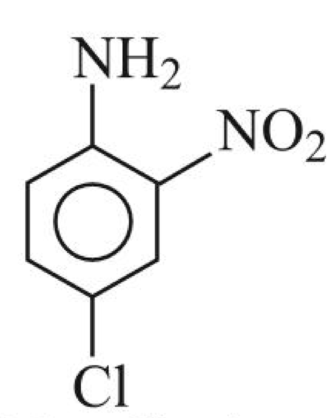
b. (A) ⇒ 

(B) ⇒ 

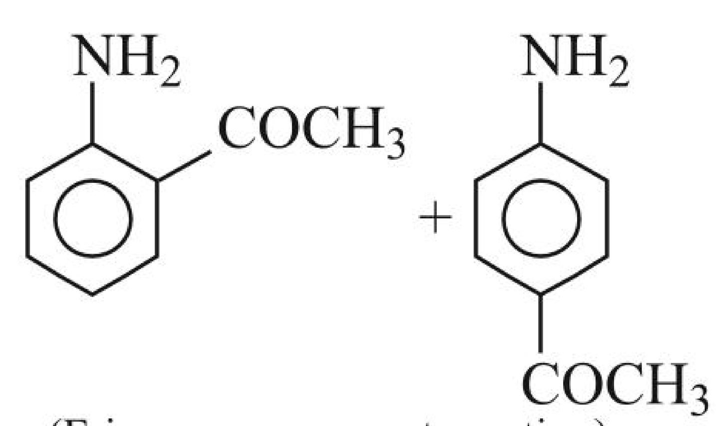
c. $NH_2CONH_2 \xrightarrow[\text{HCl/AcOH}]{\Delta} HCN + H—N{=}C{=}O$



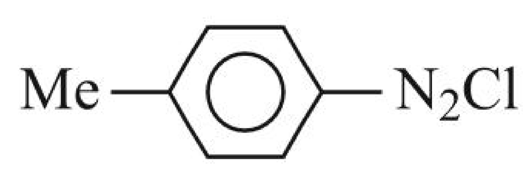
(A)

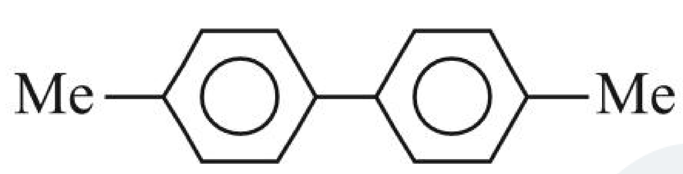
d. (A) ⇒ 

(Only *o*-Cl to intro is activated)

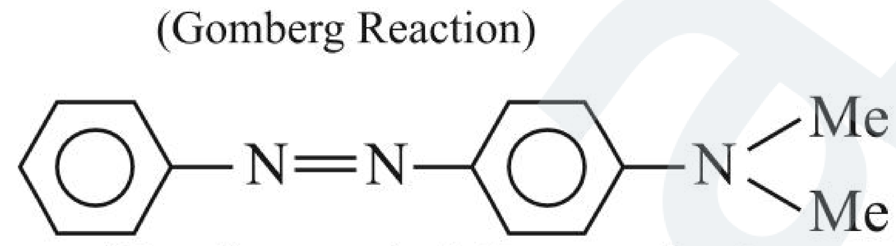
e. (A) ⇒ 

(Fries rearrangement reaction)

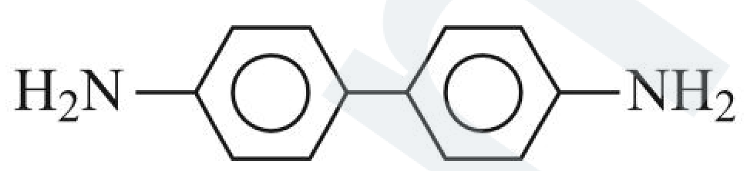
f. (A) ⇒ 

(B) ⇒ 

(Gomberg Reaction)

g. (A) ⇒ 

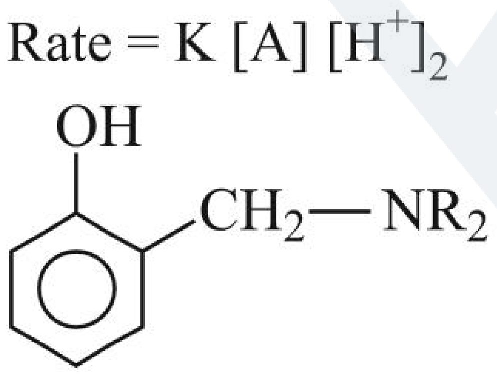
(Coupling reaction) (Butter yellow)

h. (B) ⇒ 

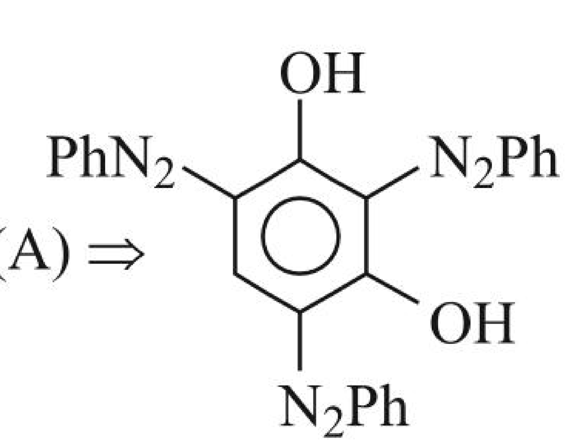
(Benzidine)

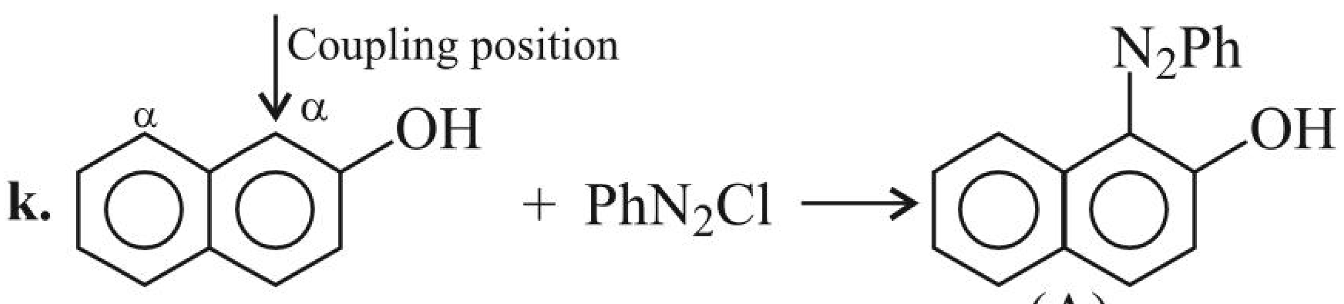
(Benzidine rearrangement reaction)

Rate = K [A] $[H^+]_2$

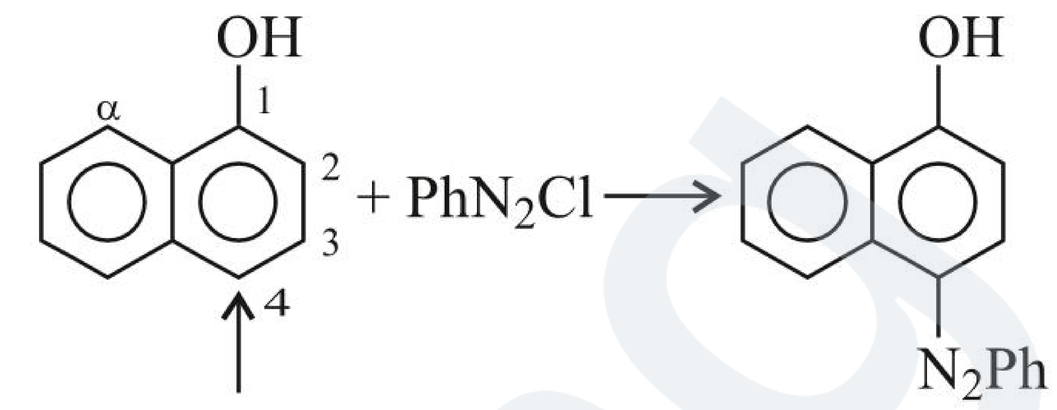
i. 

(Mannich reaction)

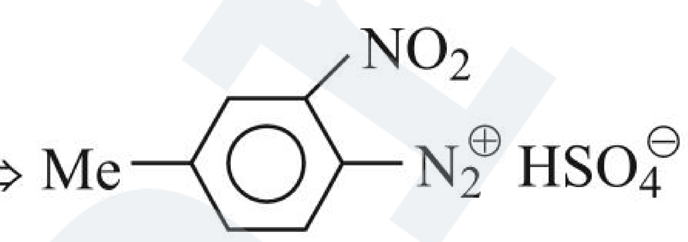
j. (A) ⇒ 

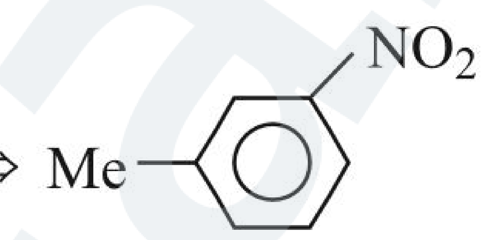
k. 

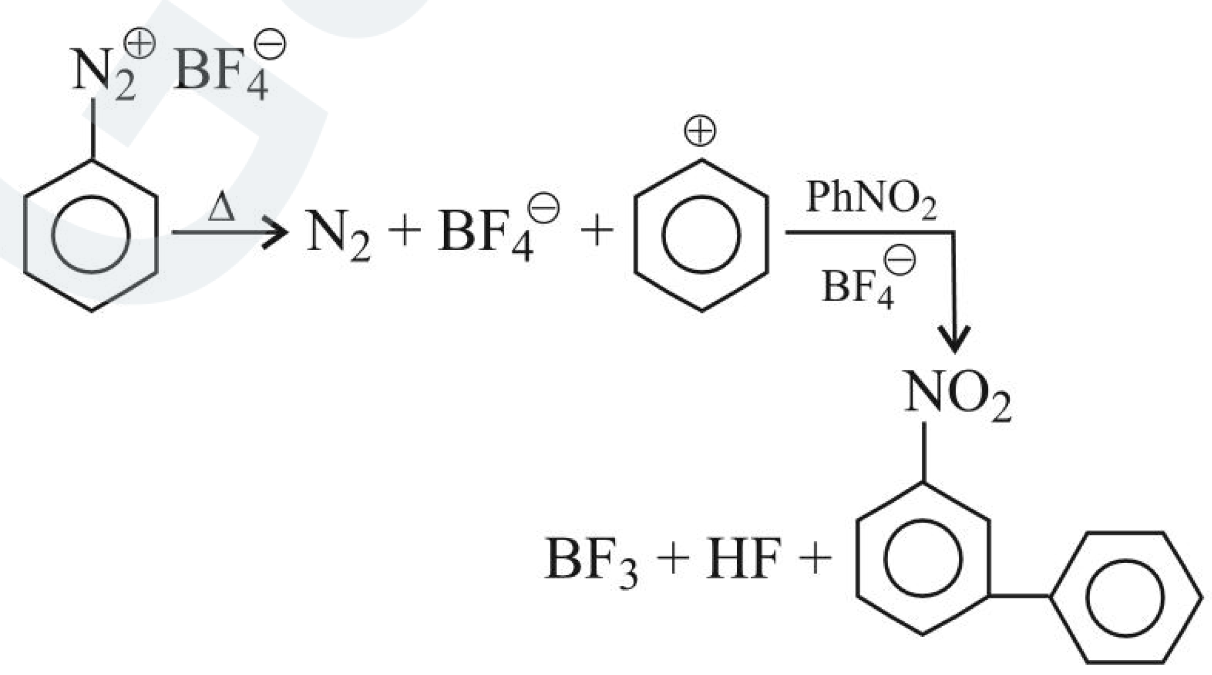
(β-Naphthol) (A) (Coupling at α)



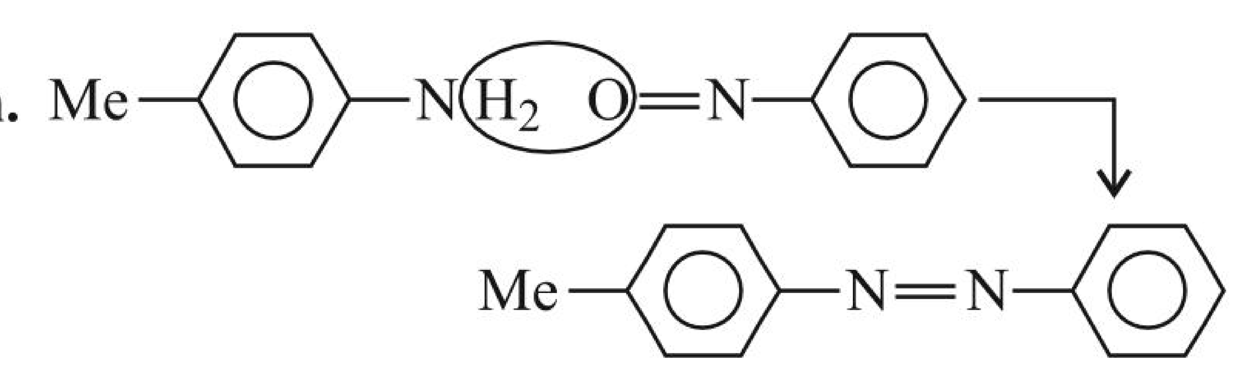
(α-Naphthol) (B) (Coupling at C-4)

l. (A) ⇒ 

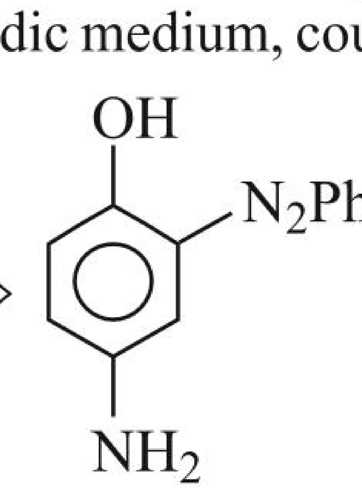
(B) ⇒ 

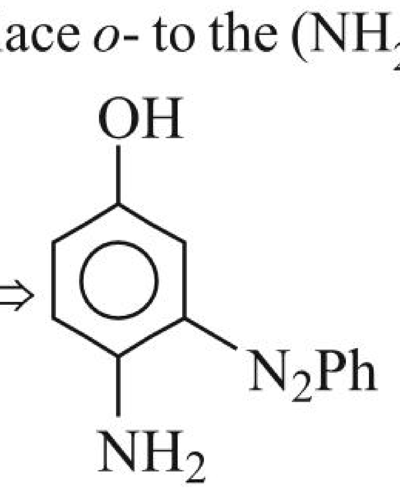
m. 

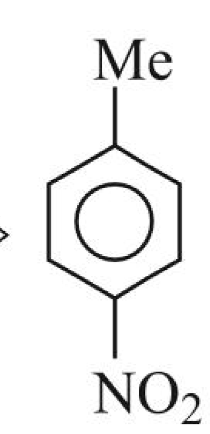
(*m*-Directing)

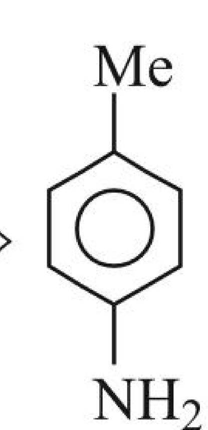
n. 

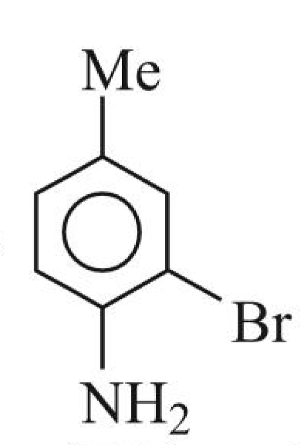
o. In basic medium, coupling takes place *o*- to the (OH) group, and in acidic medium, coupling take place *o*- to the (NH_2) group.

(A) ⇒ 

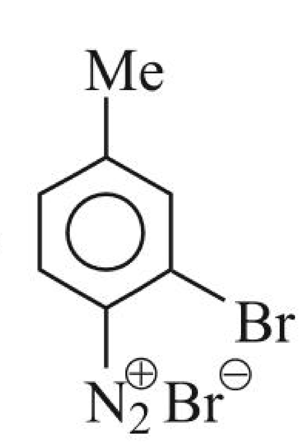
(B) ⇒ 

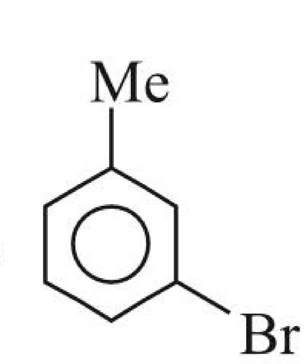
p. (A) ⇒ 

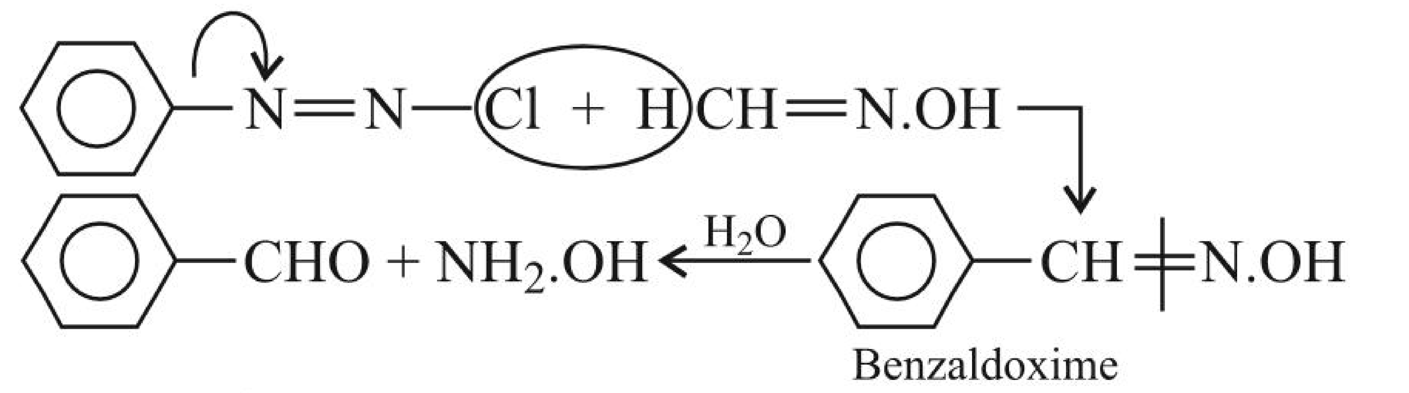
(B) ⇒ 

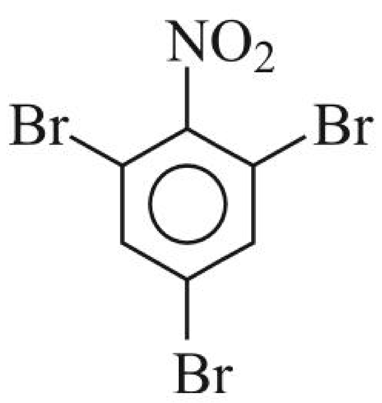
(C) ⇒ 

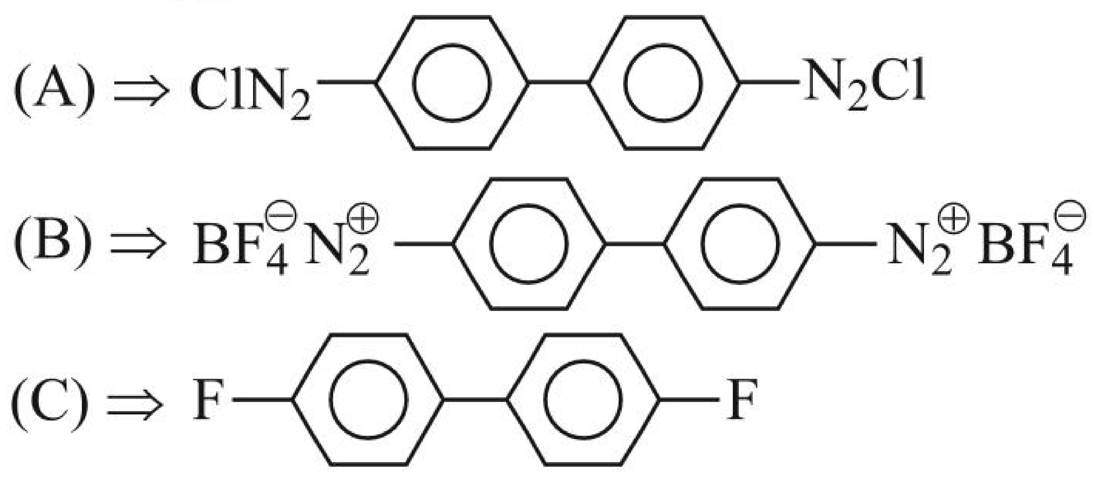
(*o*- to (NH_2) group)

(D) ⇒ 

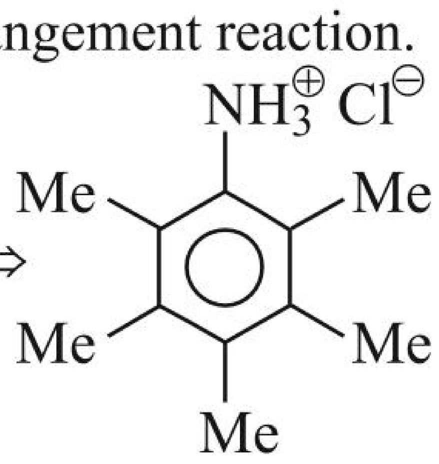
(E) ⇒ 

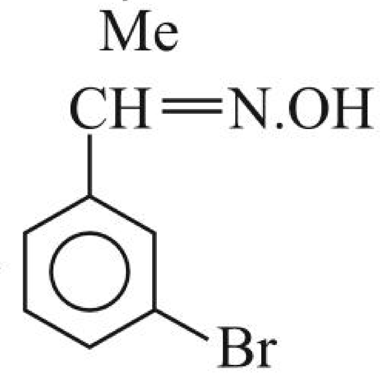
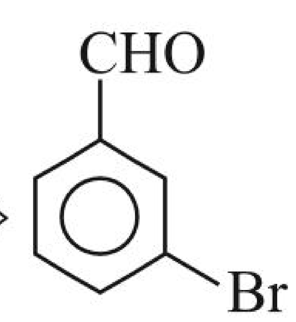
q. 

r. 

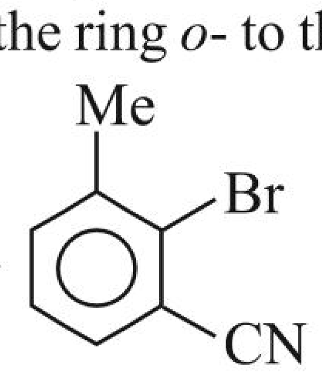
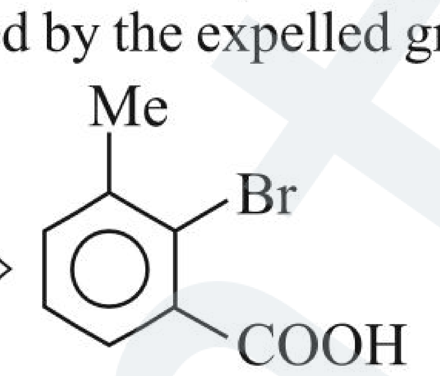
s. 

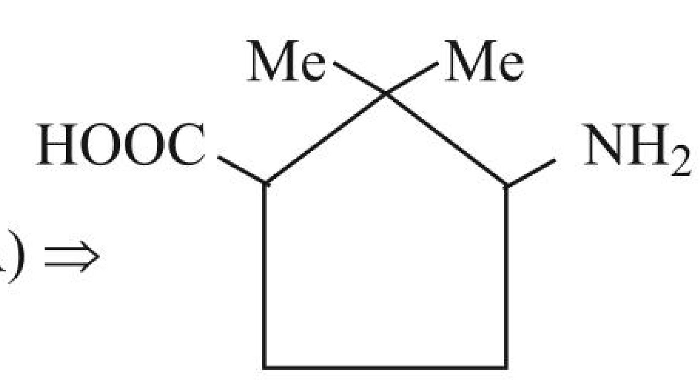
t. Migration of Me group from N atom to C atom (in benzene nucleus) takes place in steps. This is called Hofmann–Martius rearrangement reaction.

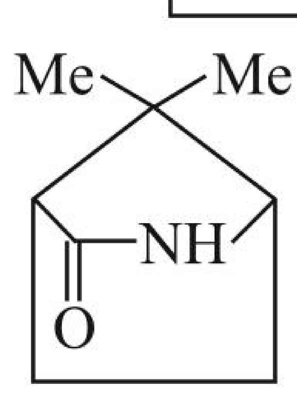
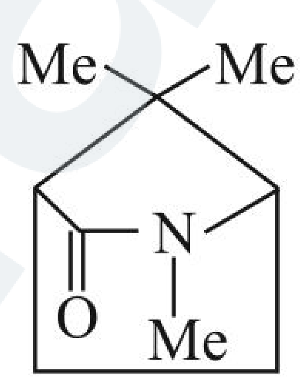
(A) ⇒ 

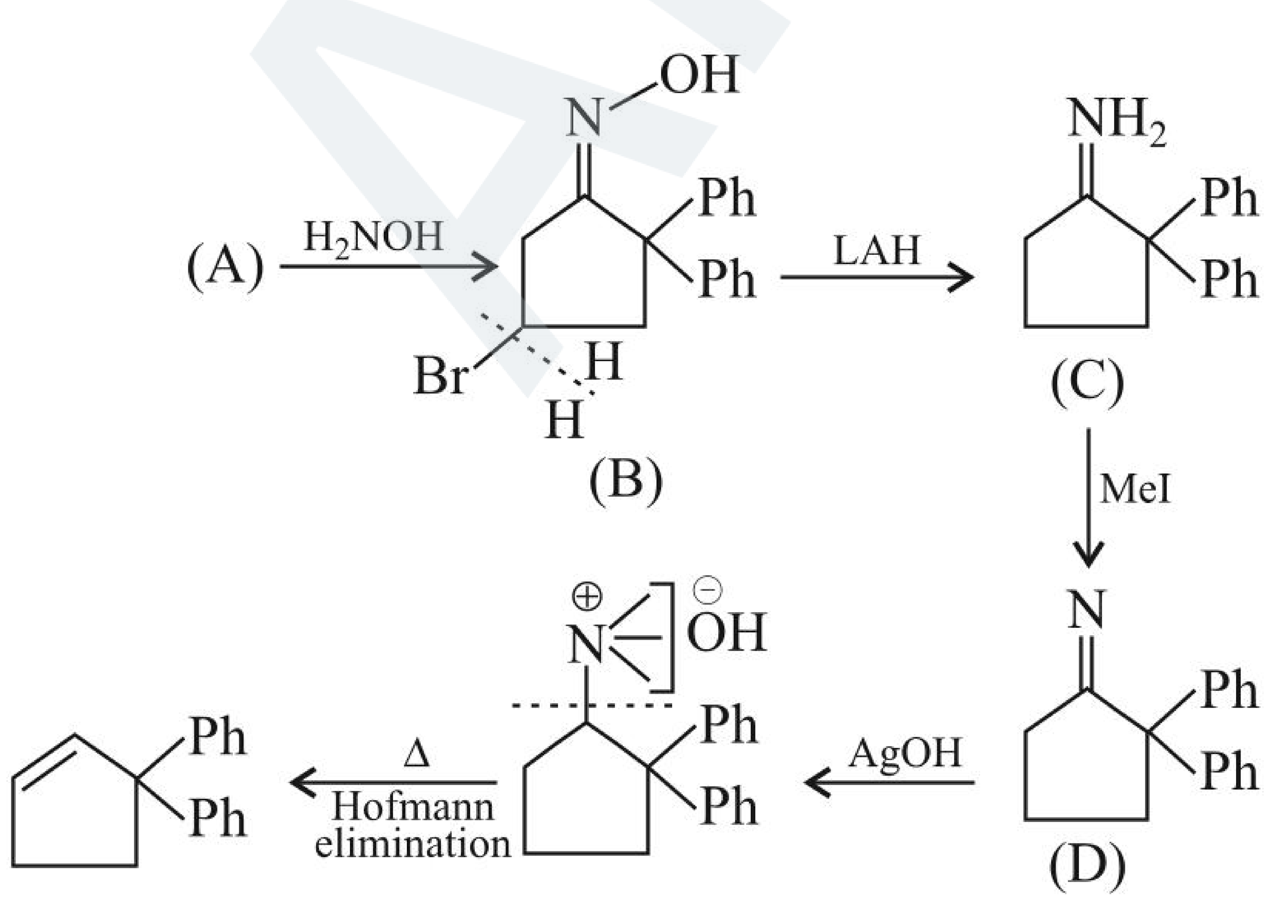
u. (A) ⇒  (B) ⇒ 

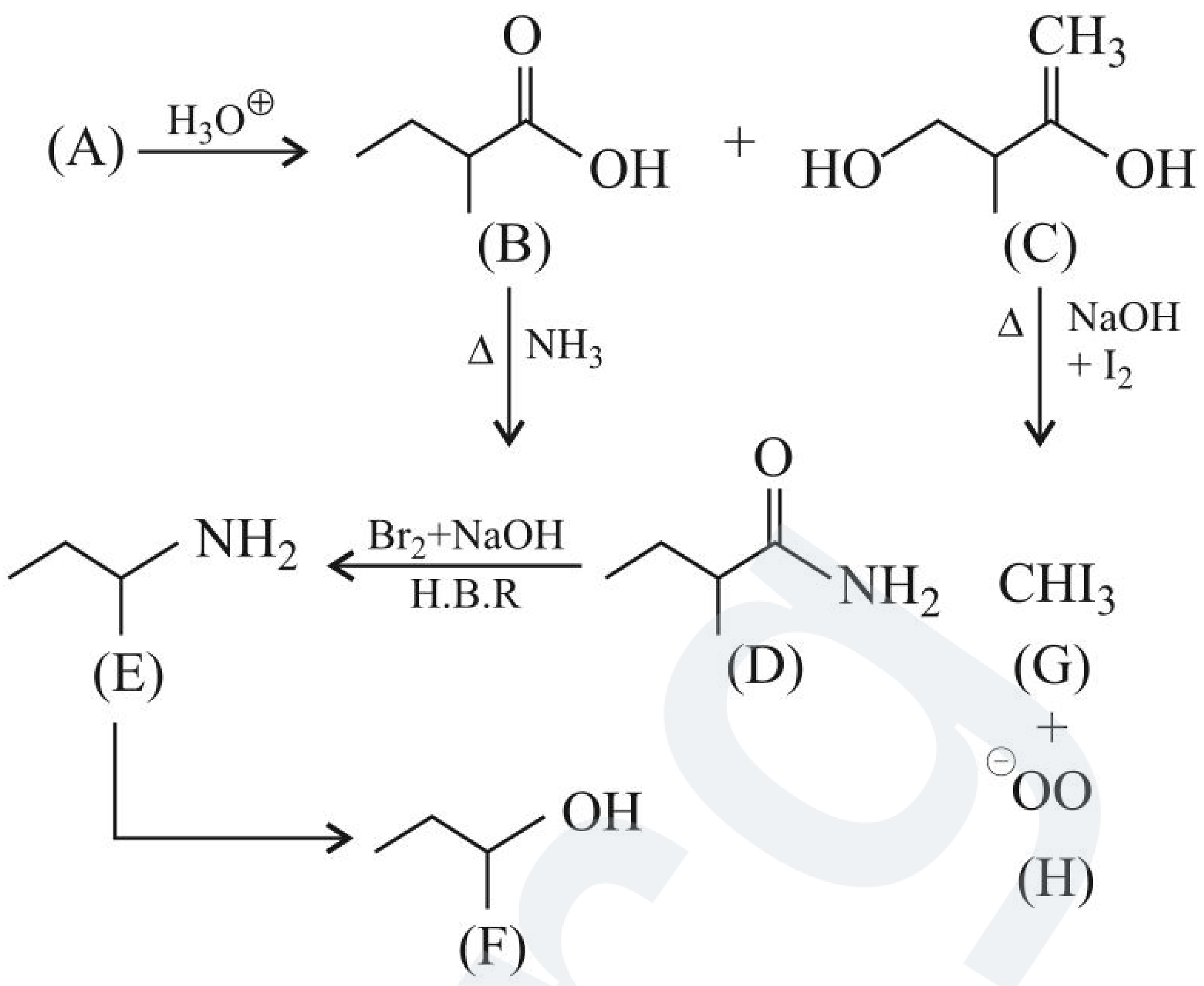
v. A von Richter reaction. When halonitro benzene in heated with KCN, then nitro group is eliminated and the (—CN) group enters the ring *o*- to the position occupied by the expelled group.

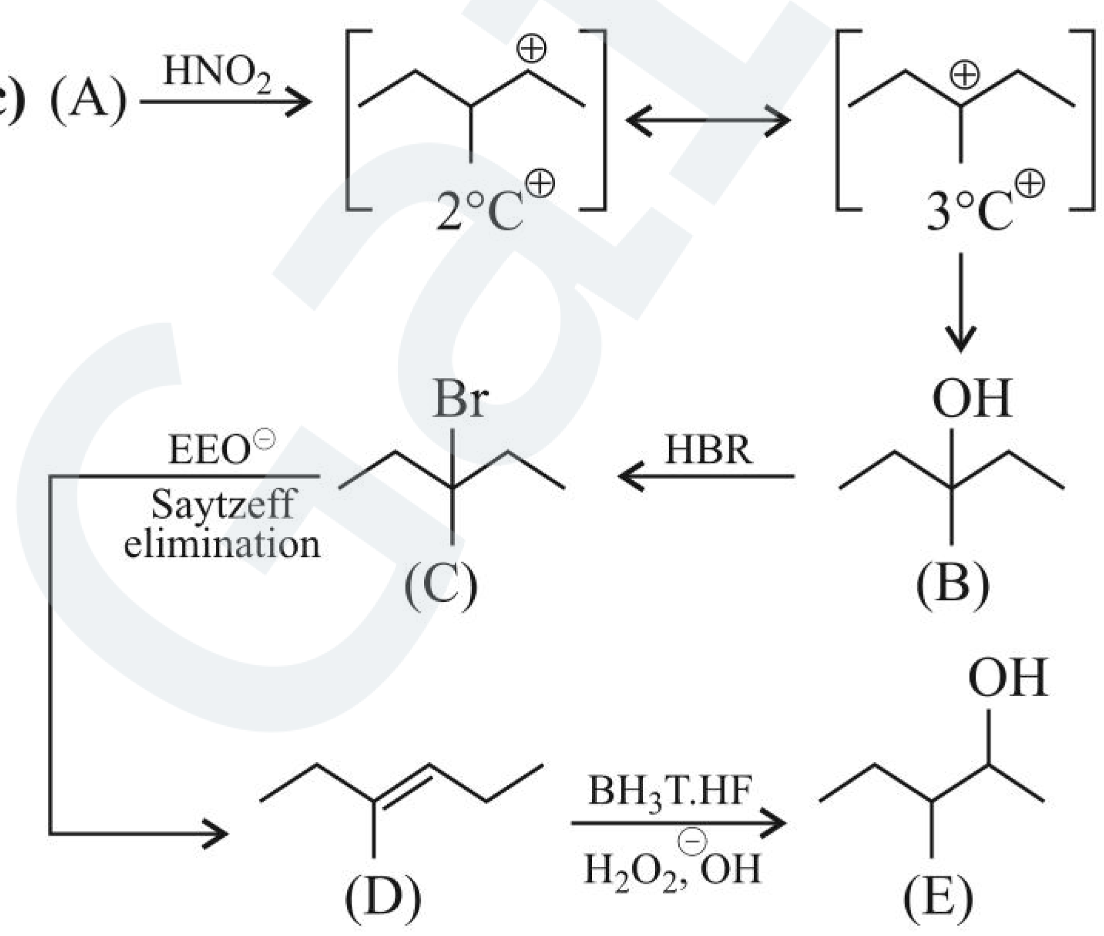
(A) ⇒  (B) ⇒ 

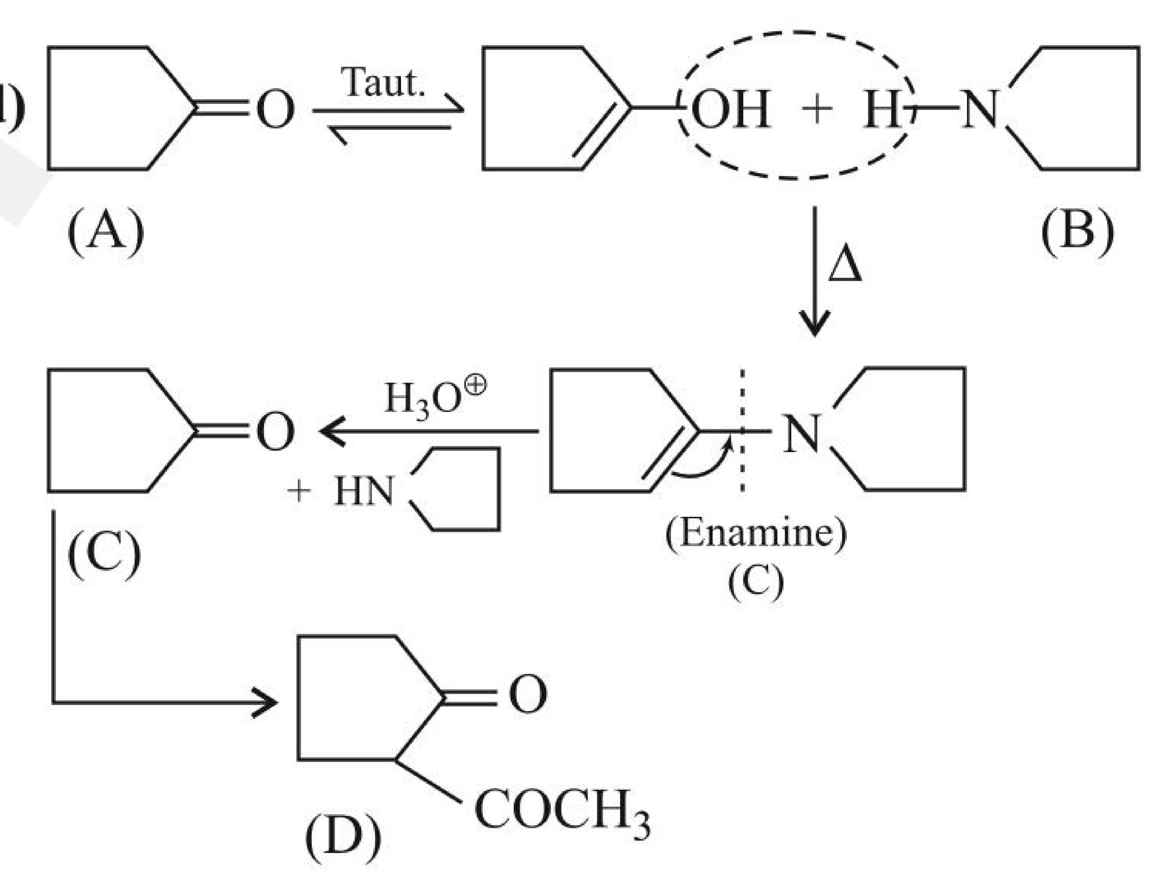
4. (A) ⇒ 

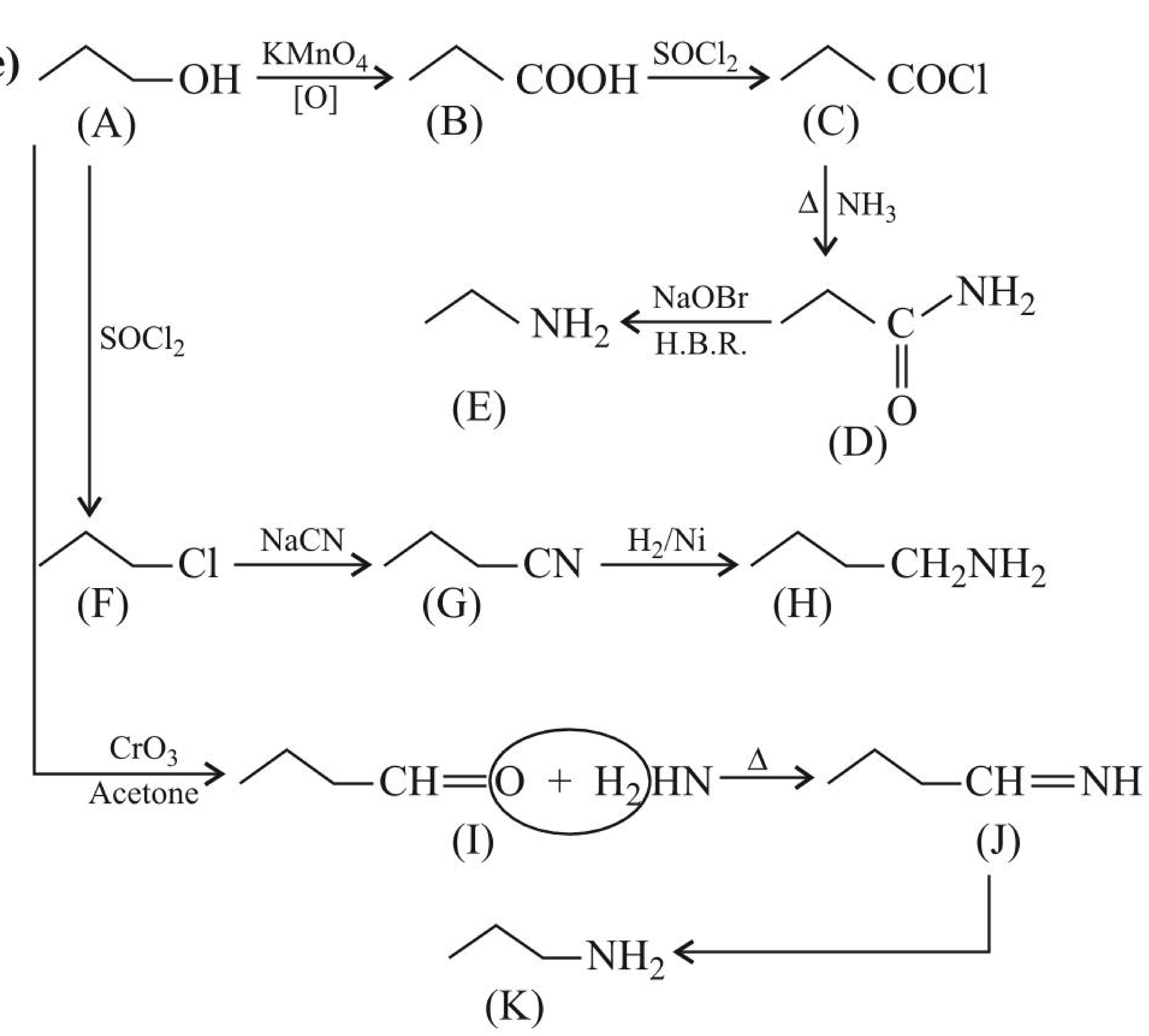
(B) ⇒  (C) ⇒ 

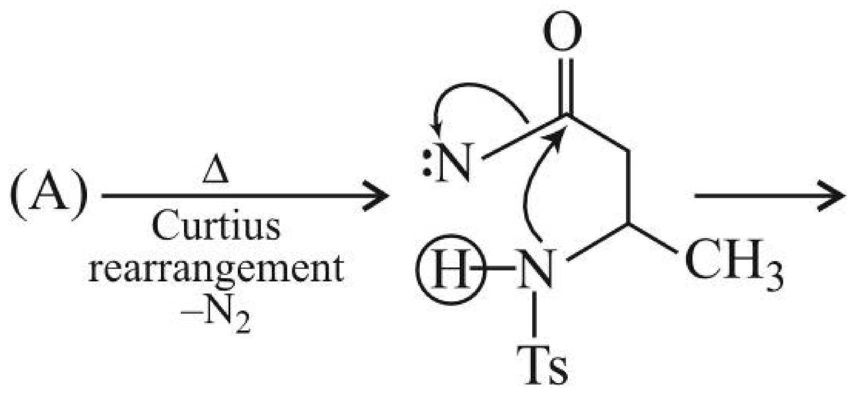
5. (a) 

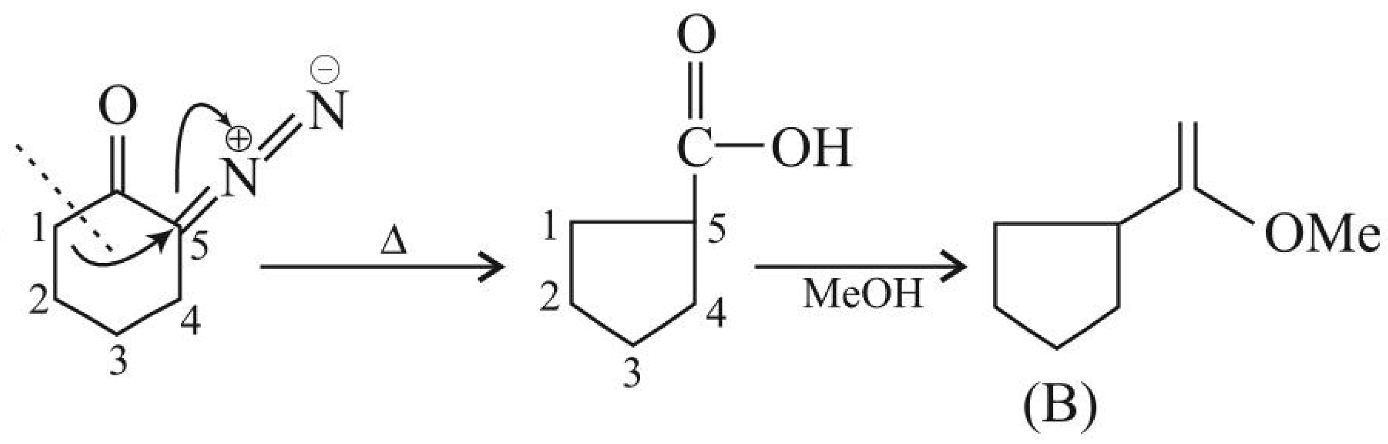
(b) 

(c) 

(d) 

(e) 

(f) 

(g) 

Exercises

Single Correct Answer Type

1. (4) It is an example of Leukart reaction .
(Refer to section 7.6)

$$\begin{matrix} H_3C \\ H_5C_2 \end{matrix}\!\!>C=O + H-\overset{\overset{O}{\|}}{C}-N(CH_3)_2$$

Dimethyl formamide (DMF)

$$\downarrow \Delta$$

$$\begin{matrix} H_3C \\ H_5C_2 \end{matrix}\!\!>CH-N(CH_3)_2 + CO_2$$

2. (3) It is an example of Leukart reaction .
(Refer to section 7.6)

$$\underset{\text{Acetone}}{(CH_3)_2C=O} + \underset{\text{Ammonium formate}}{HCOONH_4}$$

$$\downarrow 180^\circ - 200^\circ C\ \Delta$$

$$H_3C-\underset{\underset{NH_2}{|}}{CH}-CH_3 + H_2O + CO_2$$

(Propan-2-amine)

3. (3) It is an example Ritter Reaction.
(Refer to section 7.5)

$$(CH_3)_2C=CH_2 + H_2SO_4 + HCN$$

$$\downarrow$$

$$\underset{1^\circ\text{ amine}}{(CH_3)_3C-NH_2} + \underset{(X)}{HCOOH}$$

4. (3) It is an example of Ritter reaction .

$$(CH_3)_3C-OH + HCN + H_2SO_4$$

$$\downarrow$$

$$\underset{1^\circ\text{ amine}}{(CH_3)_3C-NH_2} + \underset{(X)}{HCOOH}$$

5. (1)

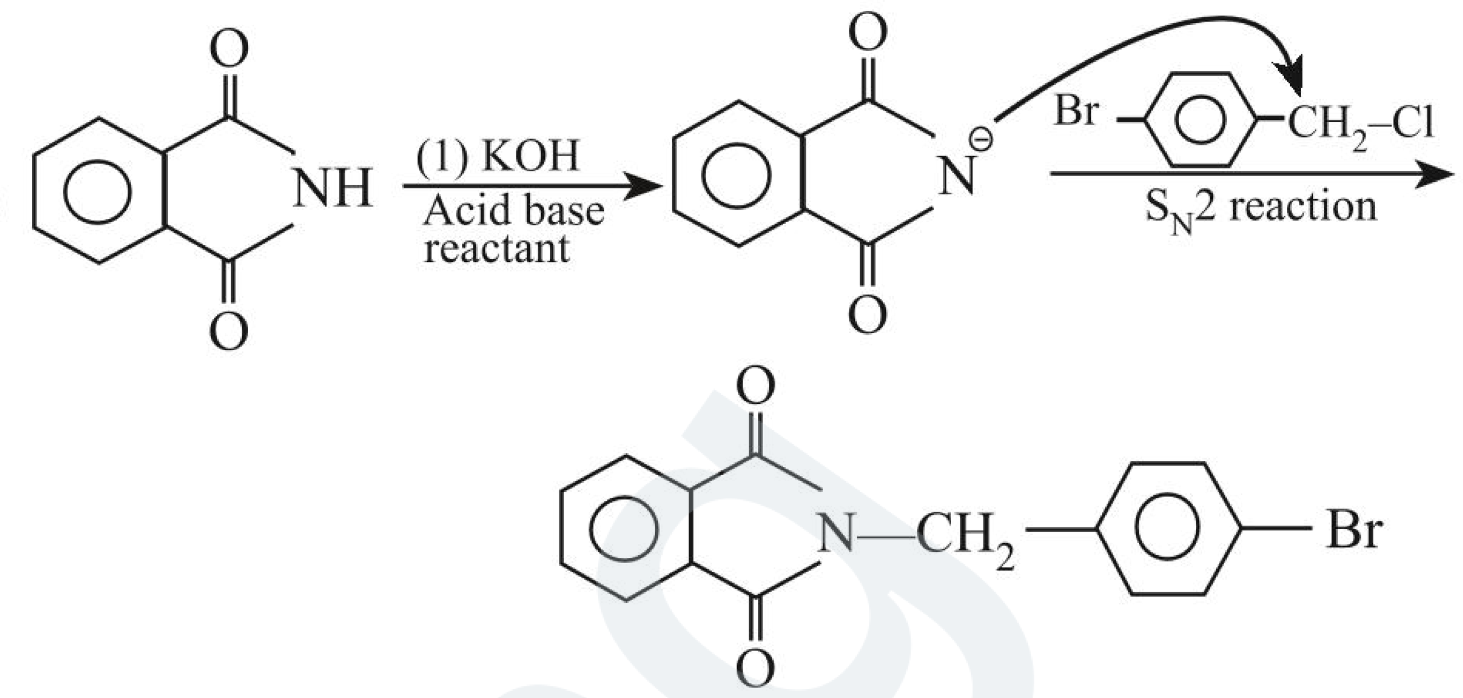
6. (4)

7. (3) RCN on hydrolysis gives RCOOH and NH_3.

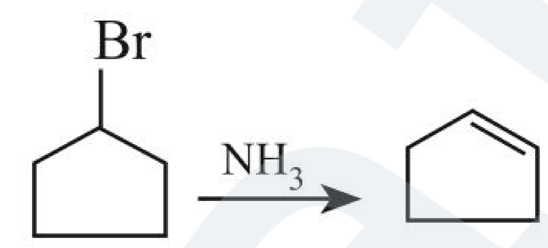
8. (4) Benzenesulphonyl chloride ($C_6H_5SO_2Cl$) is called Hinsbergs reagent.

9. (1) 1° amine or 1° aromatic amine containing EWG at *o*- and *p*-positions.

10. (3) Solvation of nucleophile is very less in presence of quarternary ammonium salt.

11. (1) 

12. (1) Reaction of 2° halide with ammonia (a base) is always accompanied by some elimination product.



13. (3) $\underset{\text{Ethanamide}}{CH_3CONH_2} \xrightarrow{Br_2 + NaOH} \underset{\text{Methyl amine}}{CH_3NH_2}$

14. (2) 4° amines are used as phase transfer catalyst and also used as cationic detergents.

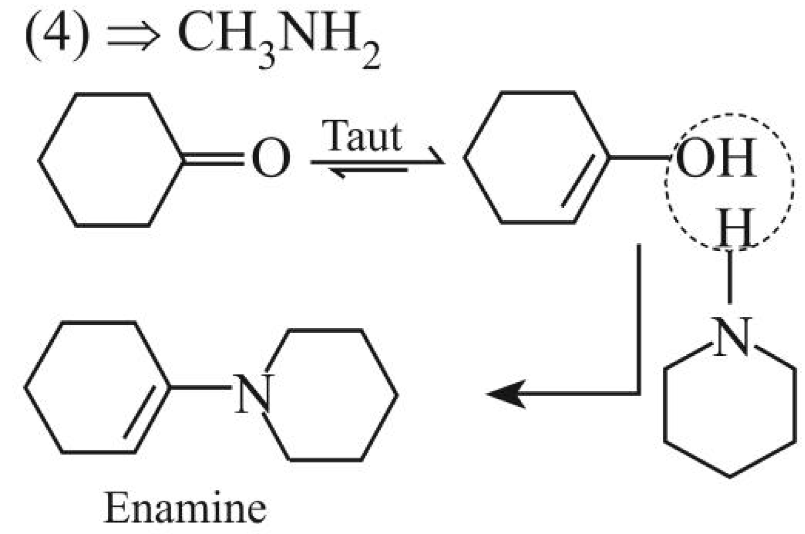
15. (3) $A \Rightarrow C_6H_5CH_2\overset{\oplus}{N}\equiv\overset{\ominus}{C} \xrightarrow{H_2O/\overset{\ominus}{O}H} \underset{(B)}{C_6H_5CH_2NH_2} + HCOOH$

16. (1)

(1) $CH_3NH_2 \xrightarrow{CHCl_3/KOH} CH_3-\overset{\oplus}{N}\equiv\overset{\ominus}{C} \xrightarrow{Sn + HCl} \underset{2^\circ\text{ amine}}{CH_3-NH-CH_3}$

(2) and (3) $\Rightarrow CH_3CN \xrightarrow[\text{or LAH}]{Sn/HCl} \underset{1^\circ\text{ amine}}{CH_3CH_2NH_2}$

(4) $\Rightarrow CH_3NH_2$

17. (1) 

18. (2)

(2) $C_2H_5CN \xrightarrow{H_3O^\oplus} C_2H_5COOH \xrightarrow{NH_3/\Delta} C_2H_5CONH_2 \xrightarrow[\Delta]{KOBr} C_2H_5NH_2$

(1) and (3) both gives ($C_2H_5CH_2NH_2$)

19. (3) **20. (1)**

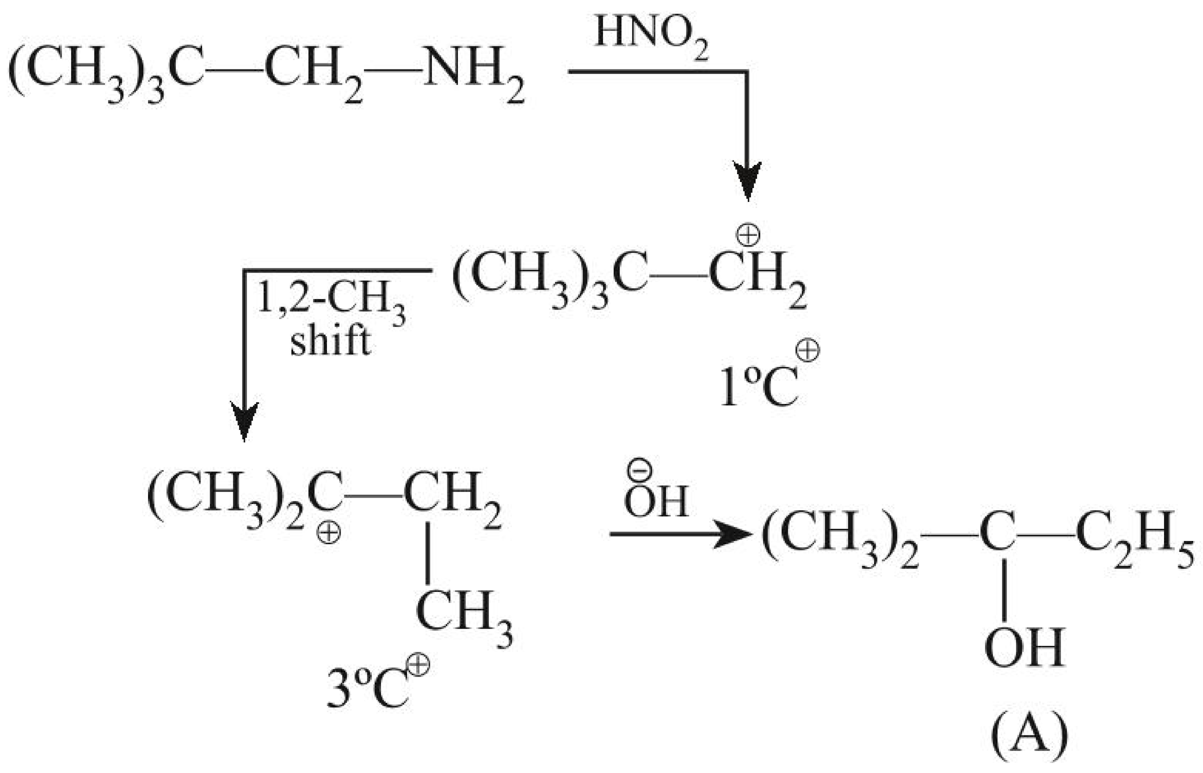
21. (2) Since (II) forms intermolecular H-bonding.

22. (3)

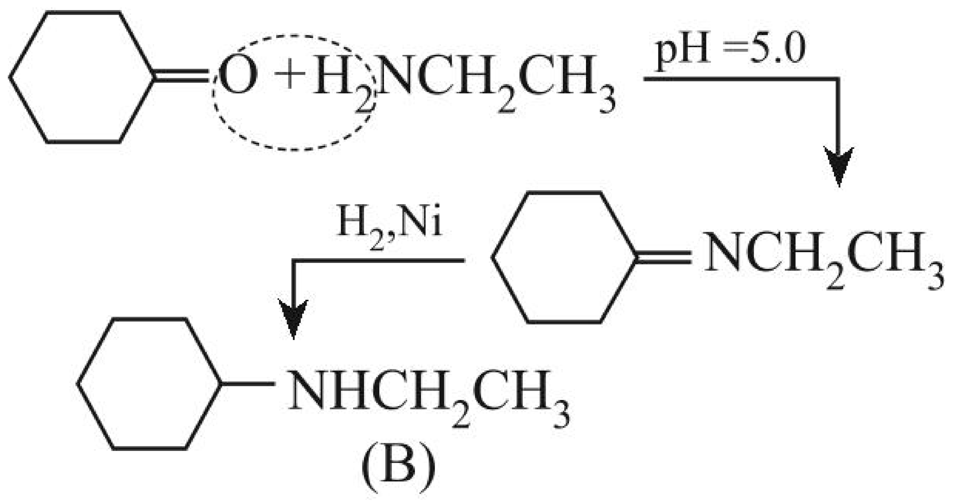
23. (2) 3° amines are volatile since they do not form intermolecular H-bonding.

24. (4) **25. (3)** **26. (1)** **27. (2)** **28. (2)**

29. (3)



30. (2)



31. (2) Less EWG, more basic EWG order :
m-NO_2 (only $-I$) < p-NO_2 ($-I$ & $-R$) < o–NO_2 ($-I$ & $-R$) but $-I$ at o- > $-I$ at p-)

32. (2)

33. (4) Three N-atoms have lone pairs of electrons.

34. (3) 2° amine forms N-nitroso derivative.

35. (4) All statements are correct.

36. (4) 1° amine to different 1° amines are not functional isomers but (1° and 2°), (1° and 3°), and (2° and 3°) of same molecular formula are functional isomers. Therefore, (1), (2), and (3) are functional isomers.

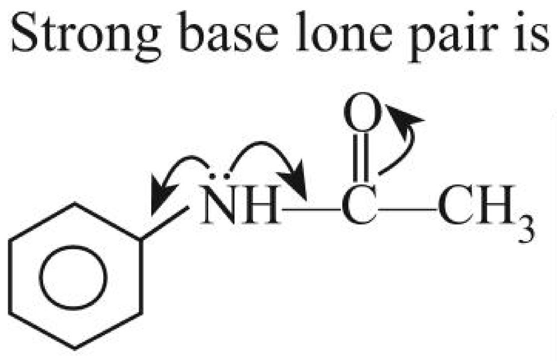
37. (2)

(4) $C_6H_5\overset{\overset{\displaystyle O}{\|}}{C}NH_2$ is weakest base because of EW power of ($>$C=O) group and resonance.

(3) Due to (–M) of NO_2 and ortho effect it is weak base.

(2) Strong base lone pair is not involved in resonance.

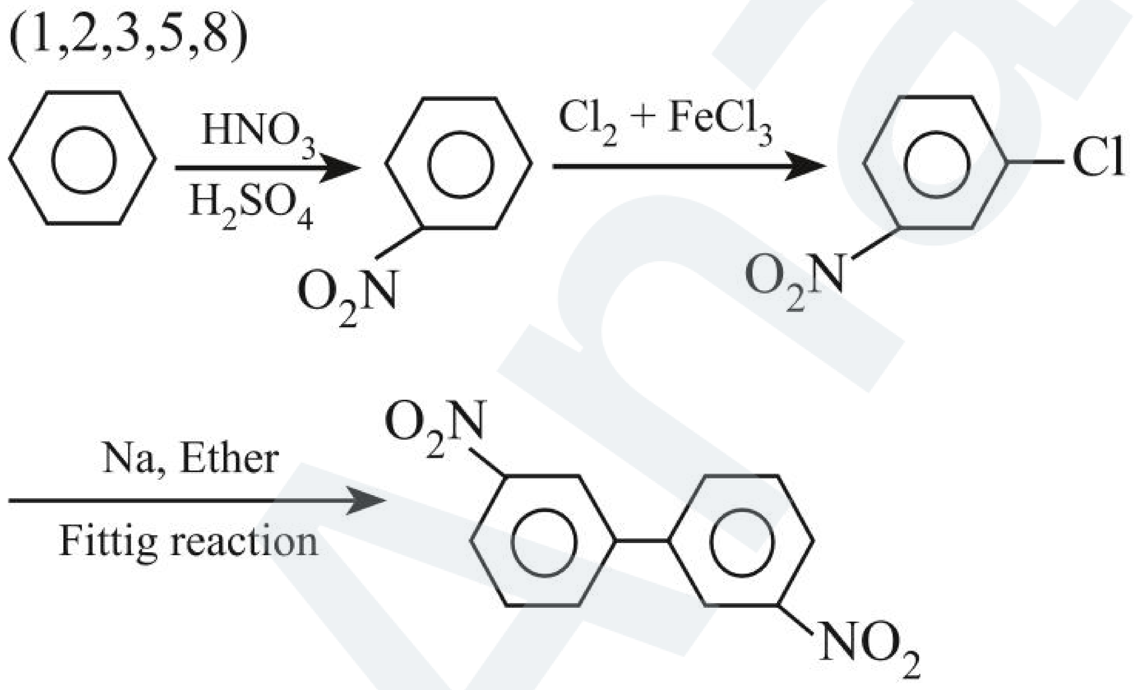
38. (4)



[Due to cross conjugation 1lone pair ē density is reduced.]

39. (3) (1,2,3,5,8)

40. (1)



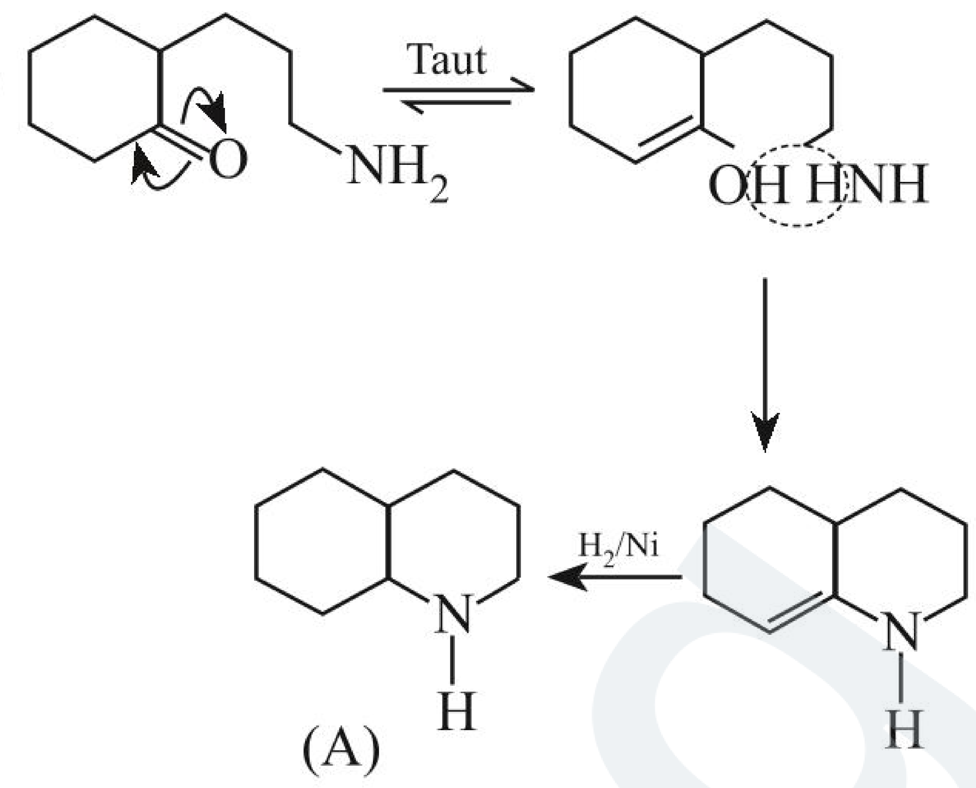
41. (4) Neutral nature of the compound indicates that it should be a nitro compound. Further zero dipole moment indicates its symmetrical structure, *i.e.*, it should be a benzene derivative having same group ($-NO_2$) in positions *para* to each other.

42. (4) As NH_2 group is more active towards acetylation.

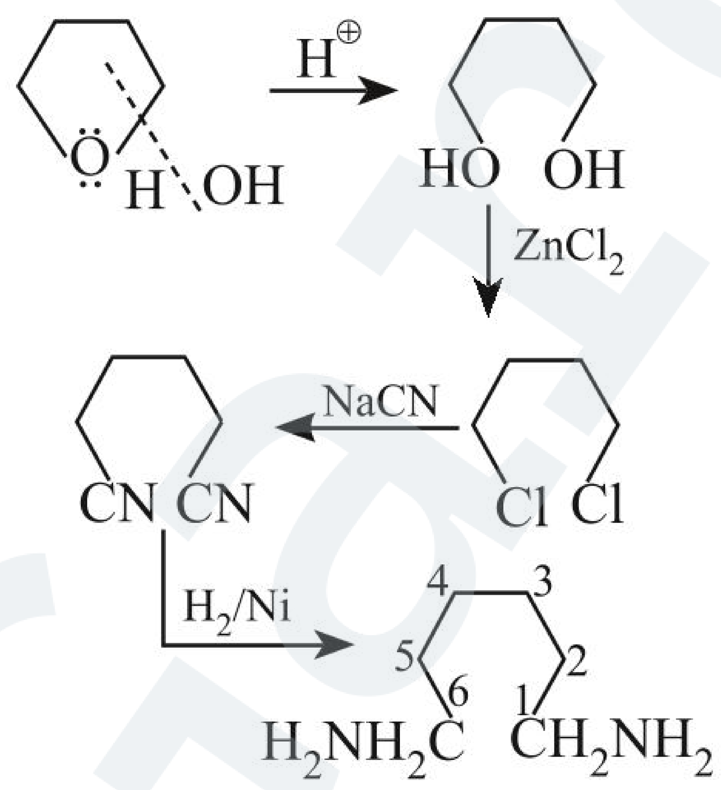
43. (2) In the Zwitter ion of sulphanilic acid, the $-SO_3^{\ominus}$ is too weakly basic (its conjugate acid $-SO_3H$ is a strong acid) to accept $H^{\oplus}$ from strong acids, hence it does not dissolve in HCl.

44. (1) Electronegativity of O, N and C follows the order :
O > N > C.

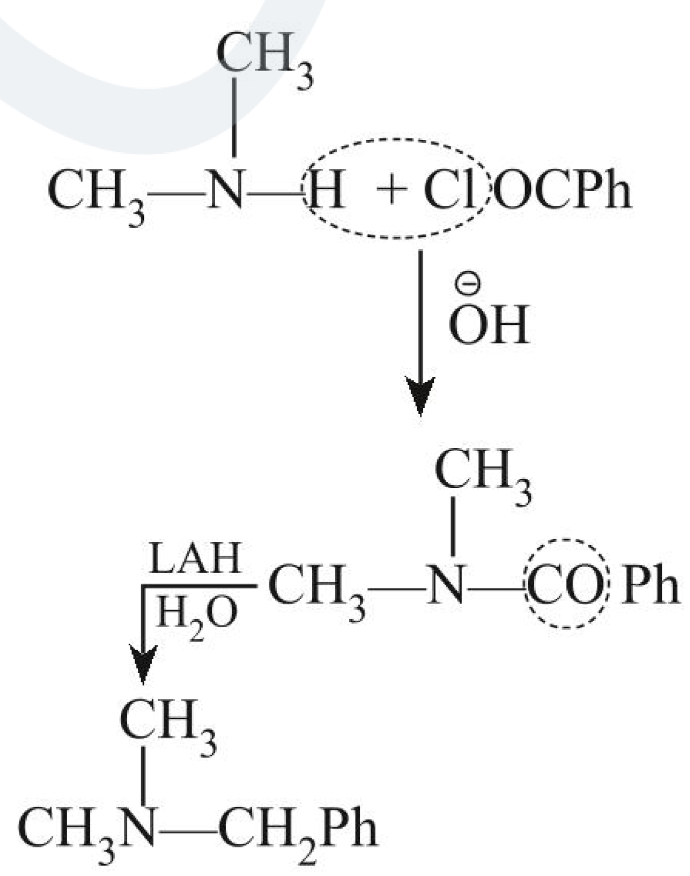
45. (3)



46. (3)

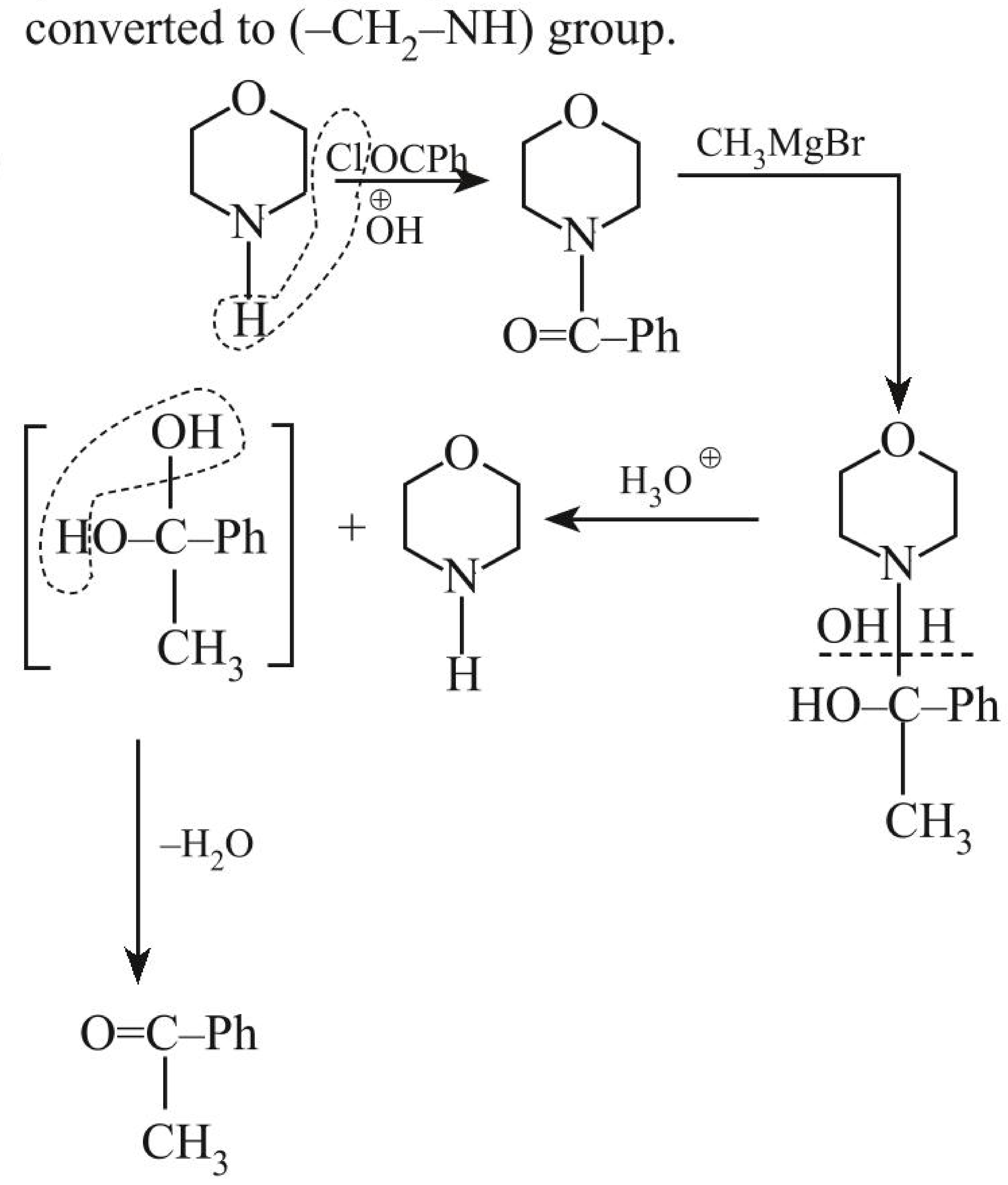


47. (2)

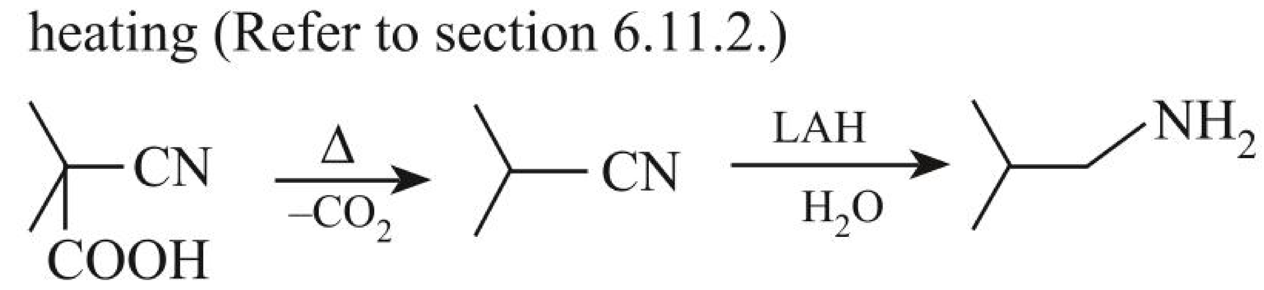


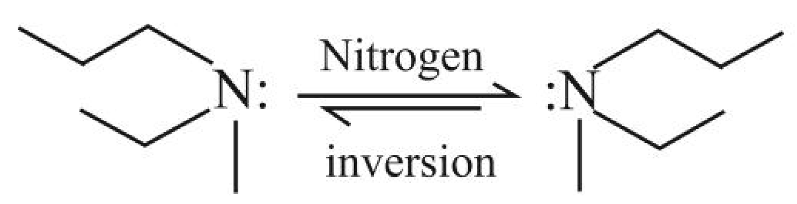
($-\overset{\overset{\displaystyle O}{\|}}{C}-NH-$) group is N-substituted amide, so by LAH it is converted to ($-CH_2-NH$) group.

48. (4)

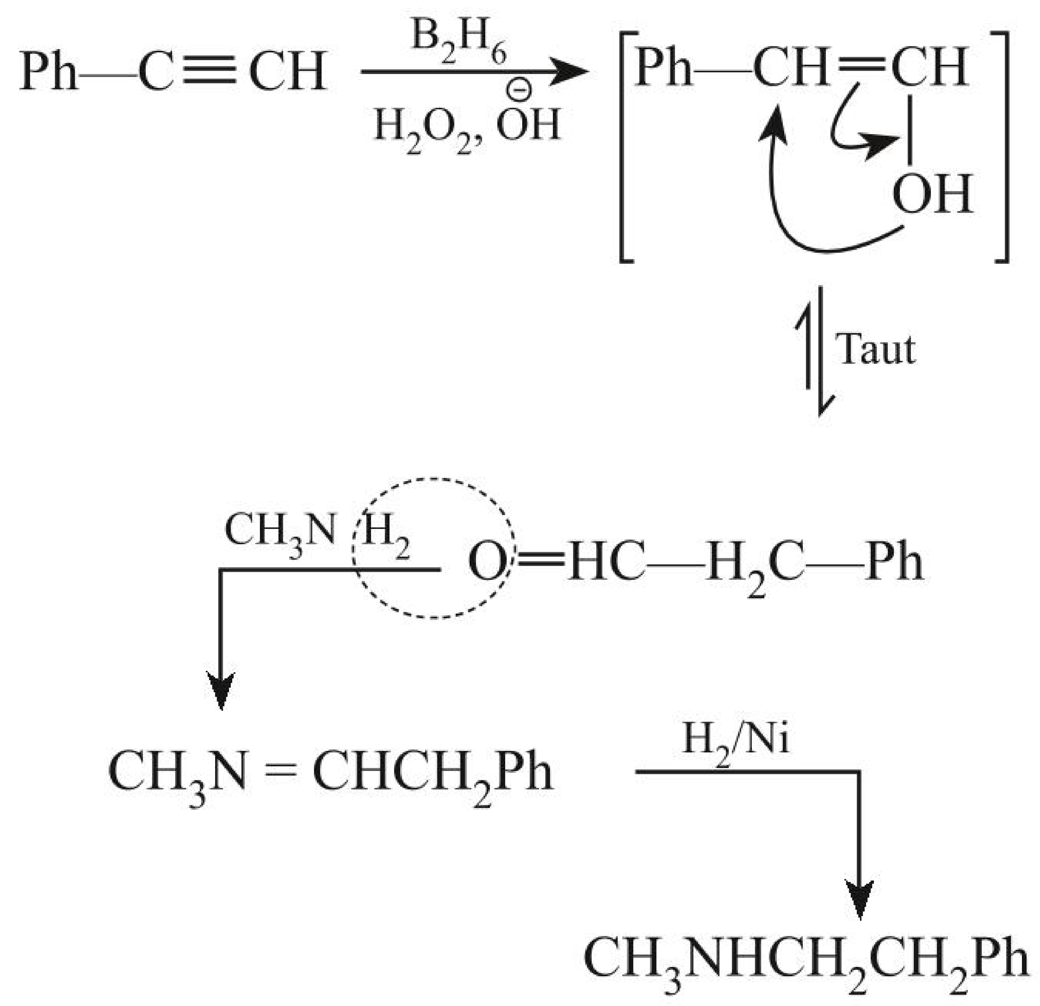


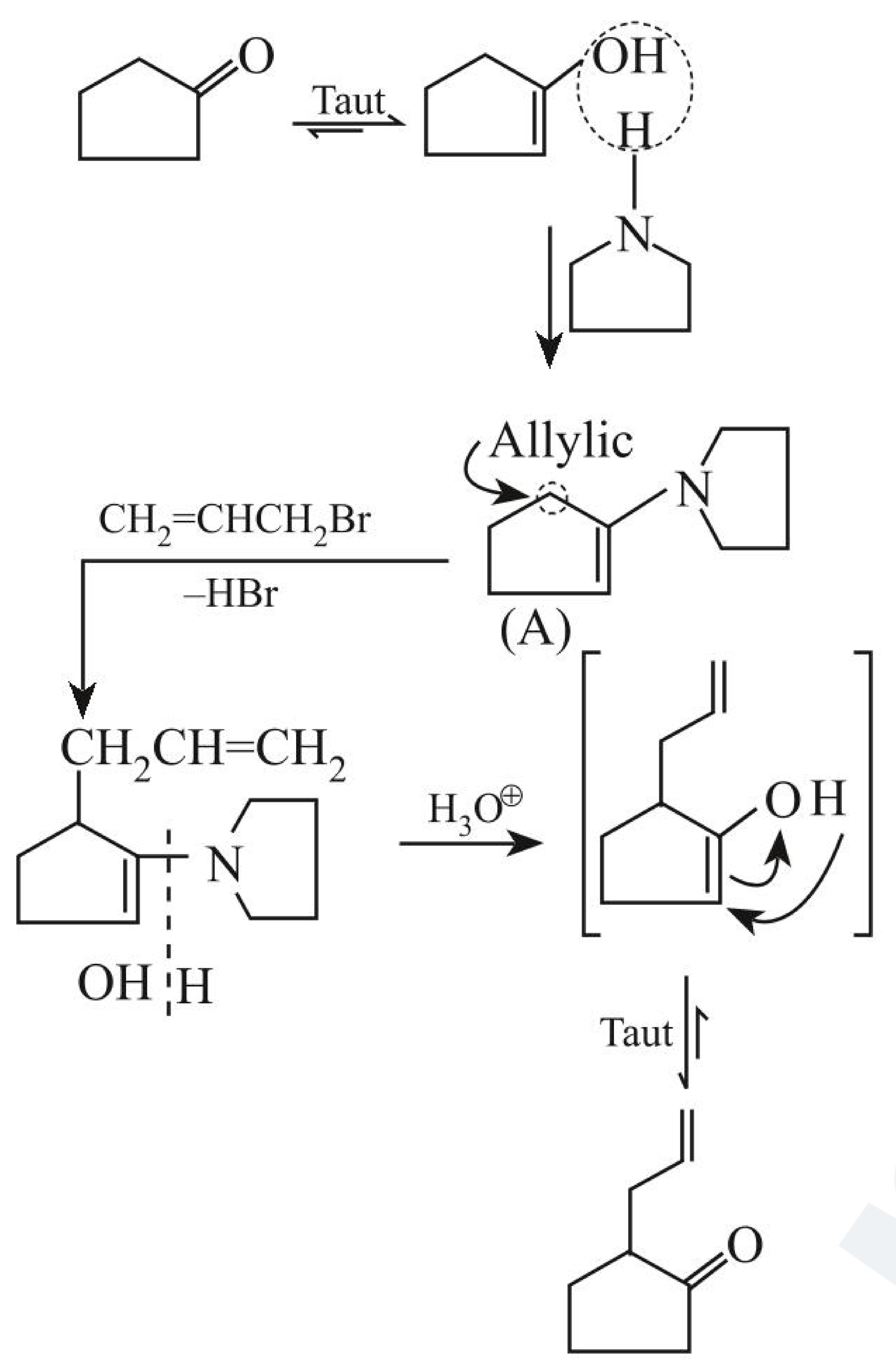
49. (1) More stronger EWG, more easily the acid is decarboxylate on heating (Refer to section 6.11.2.)



50. (1) 

N-atom has four different groups (CH_3, C_2H_5, C_3H_7 and lone pair). A rapid "umbrella" type inversion converts either of the enantiomers to a recemic mixture.

51. (3) 

52. (4) 

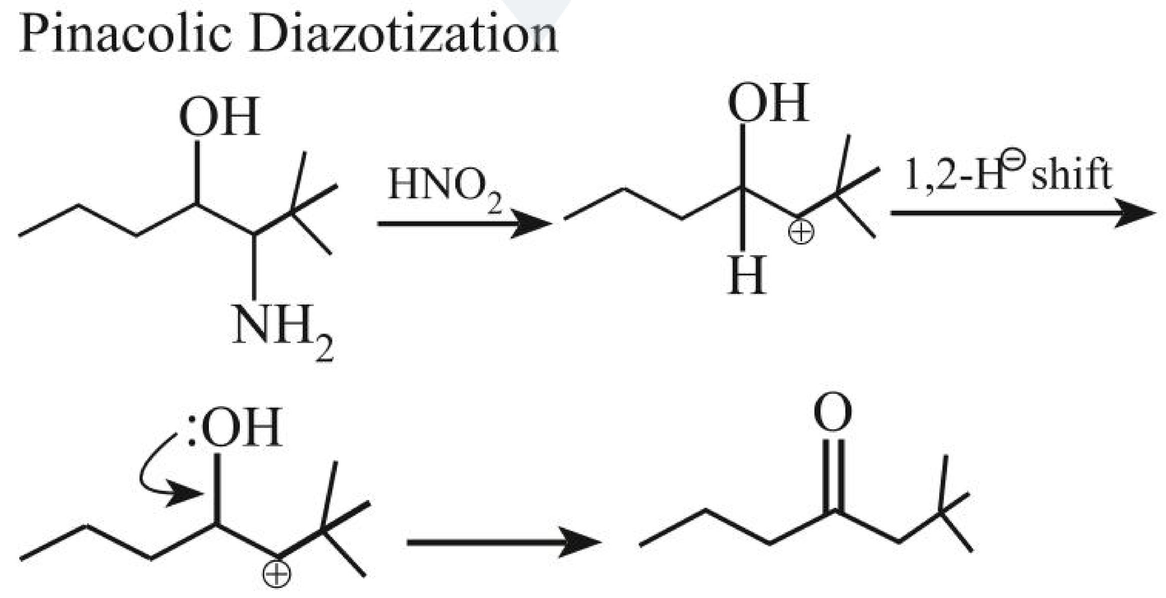
53. (3) Since n-C_4H_9Li is stronger base than the amine in (3), so amine behaves as an acid.

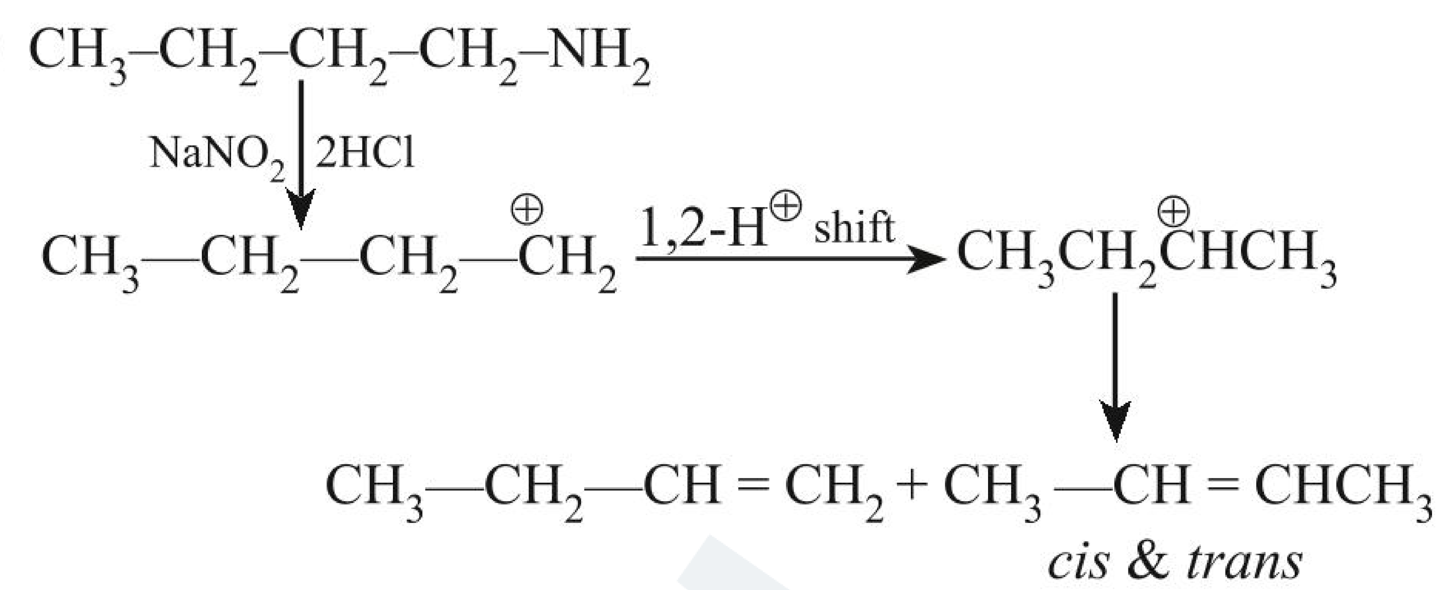
54. (2) Only primary aromatic amines undergo diazotisation followed by coupling.

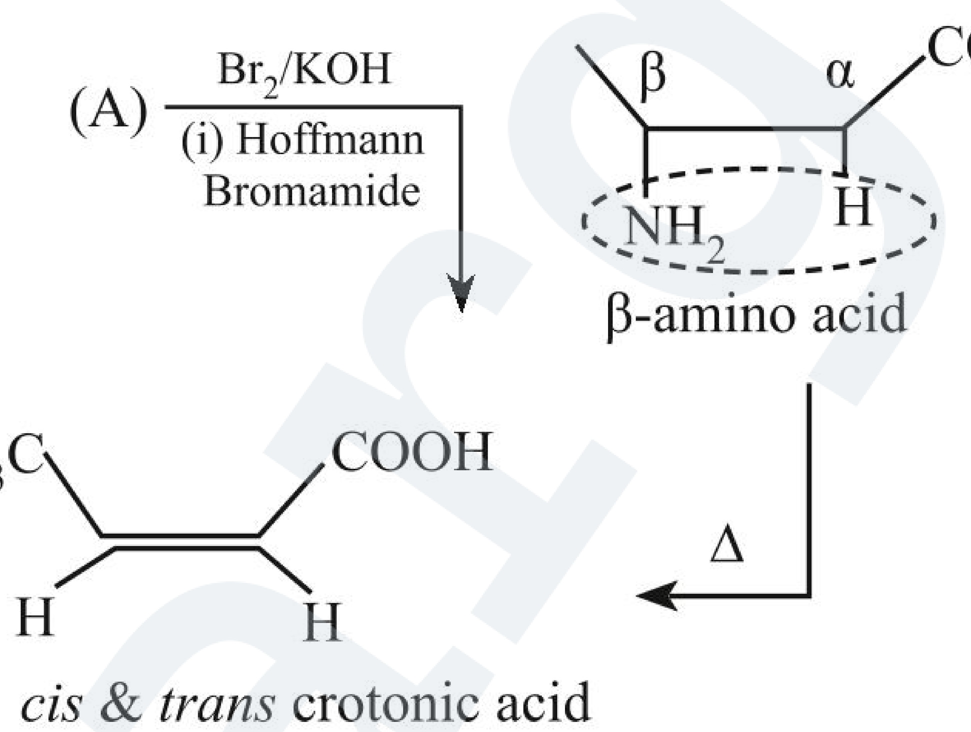
55. (2) Presence of electron withdrawing group in arene diazonium ions enhances the electrophilic character of the ion and thus increases coupling.

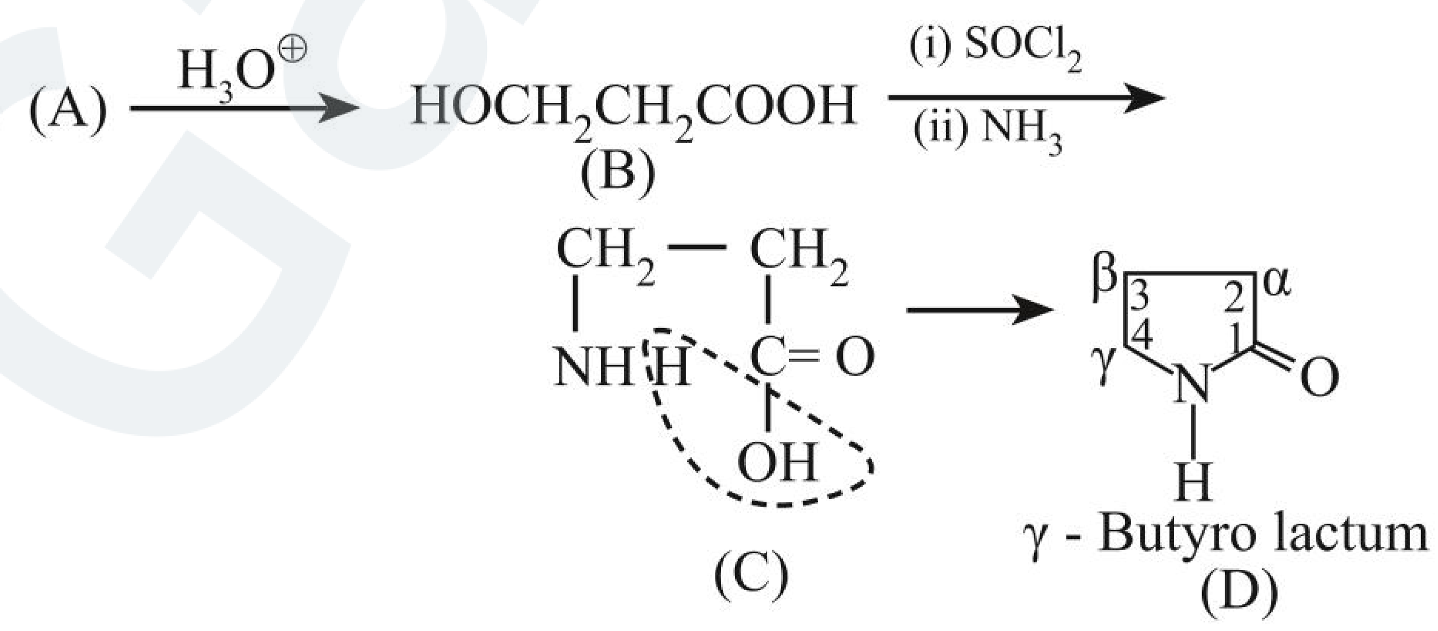
56. (3) Coupling reaction between arenediazonium cation and an aromatic compounds which bear powerful electron- releasing group like –OH, –NH_2, –NHR, or –NR_2. Hence toluene, having weak electron-releasing –CH_3 group can't couple with diazonium cation.

57. (1) Pinacolic Diazotization

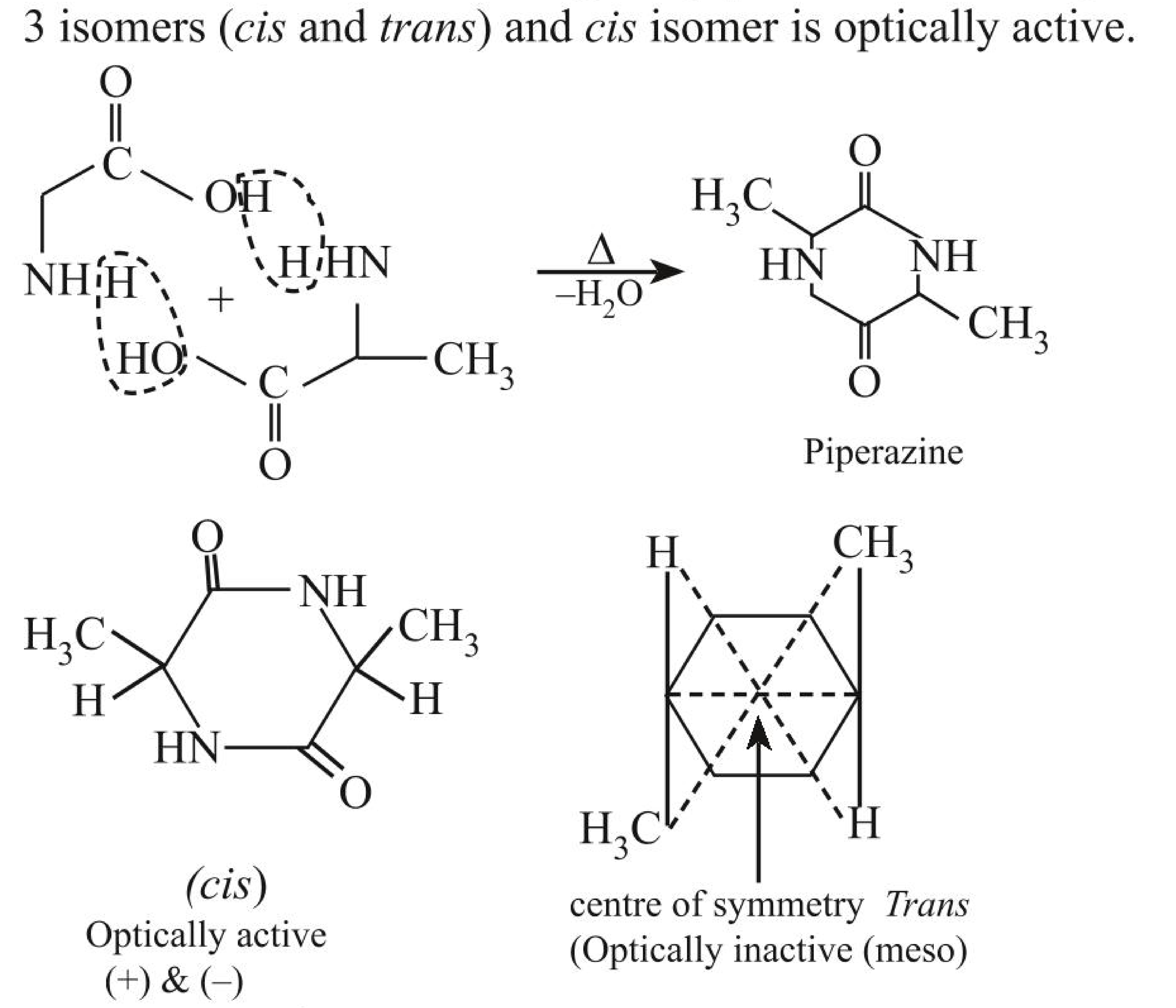


58. (4) 

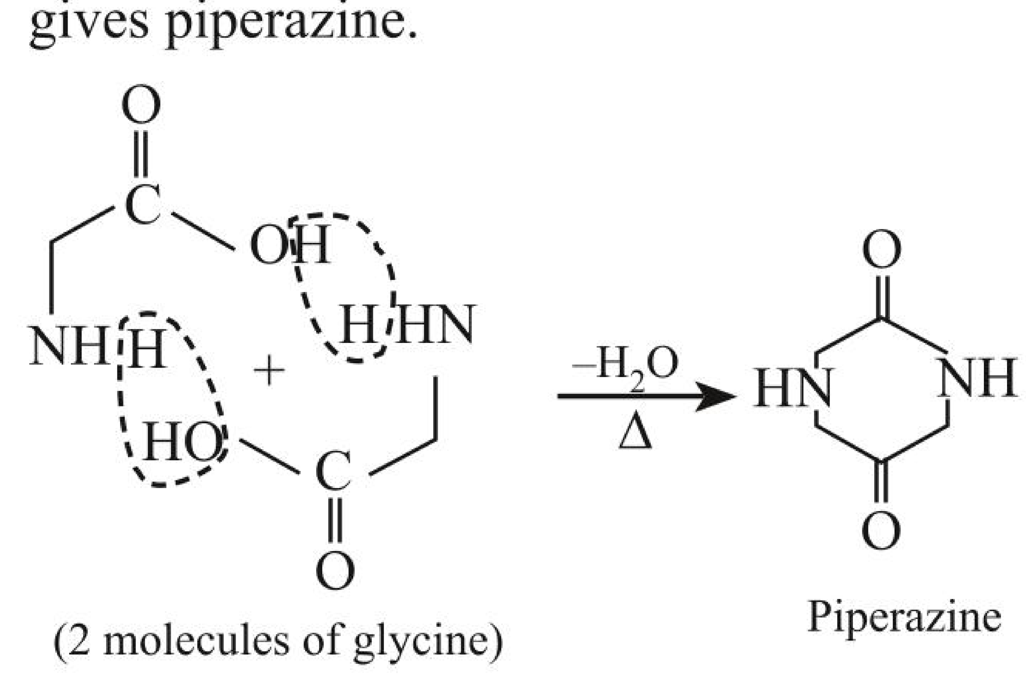
59. (2) 

60. (2) 

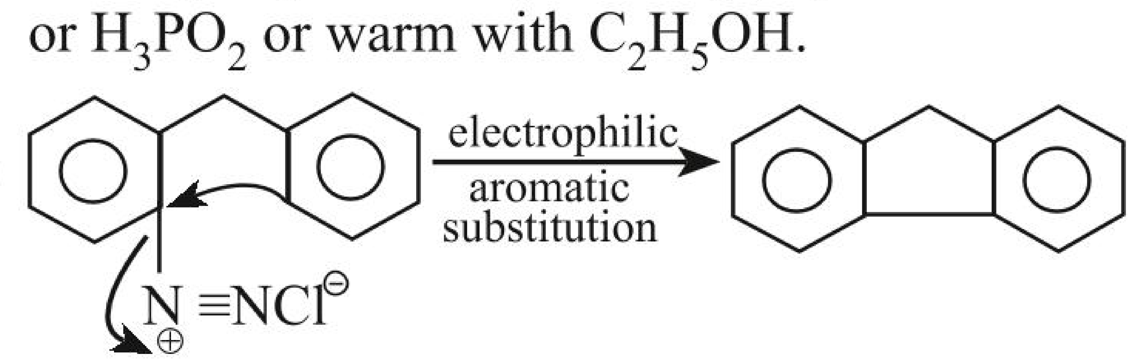
61. (3) Alanine is α-amino acid and gives piperazine on heating with 3 isomers (*cis* and *trans*) and *cis* isomer is optically active.



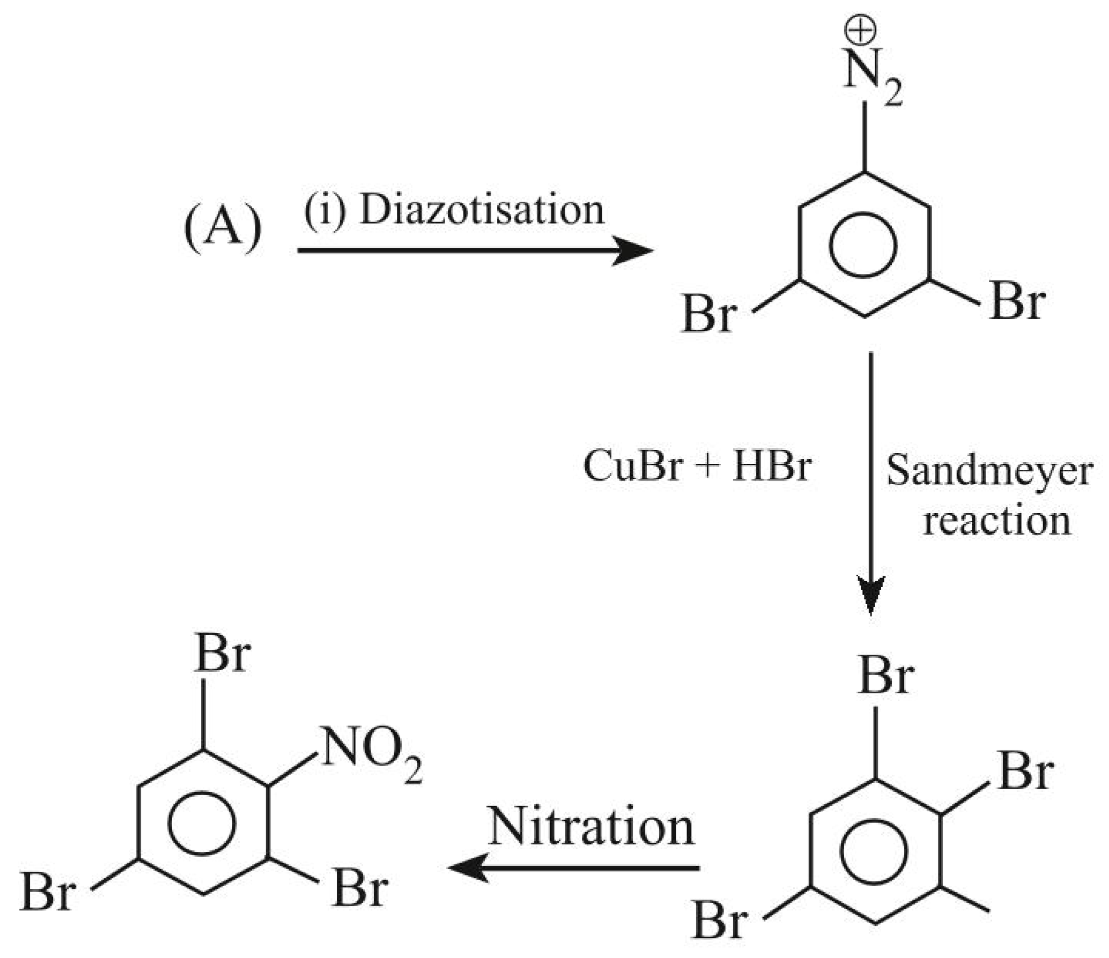
62. (2) Glycine ($NH_2\overset{\alpha}{C}H_2COOH$) is α-amino acid which on heating gives piperazine.



63. (2) Diazo group can be replaced by (H) on reduction with Na_2SnO_2 or H_3PO_2 or warm with C_2H_5OH.

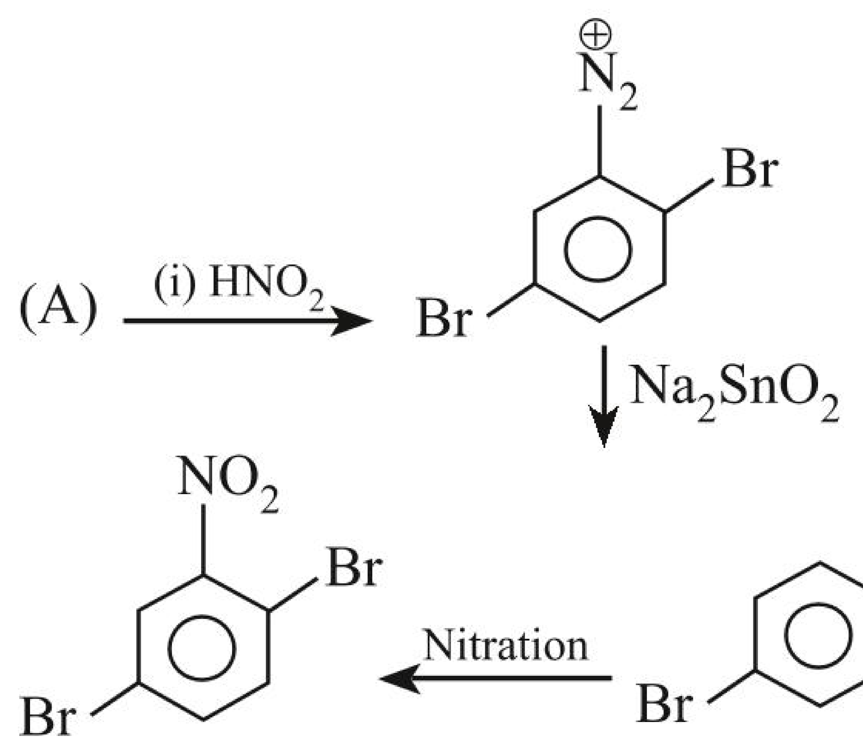
64. (2) 

65. (2)

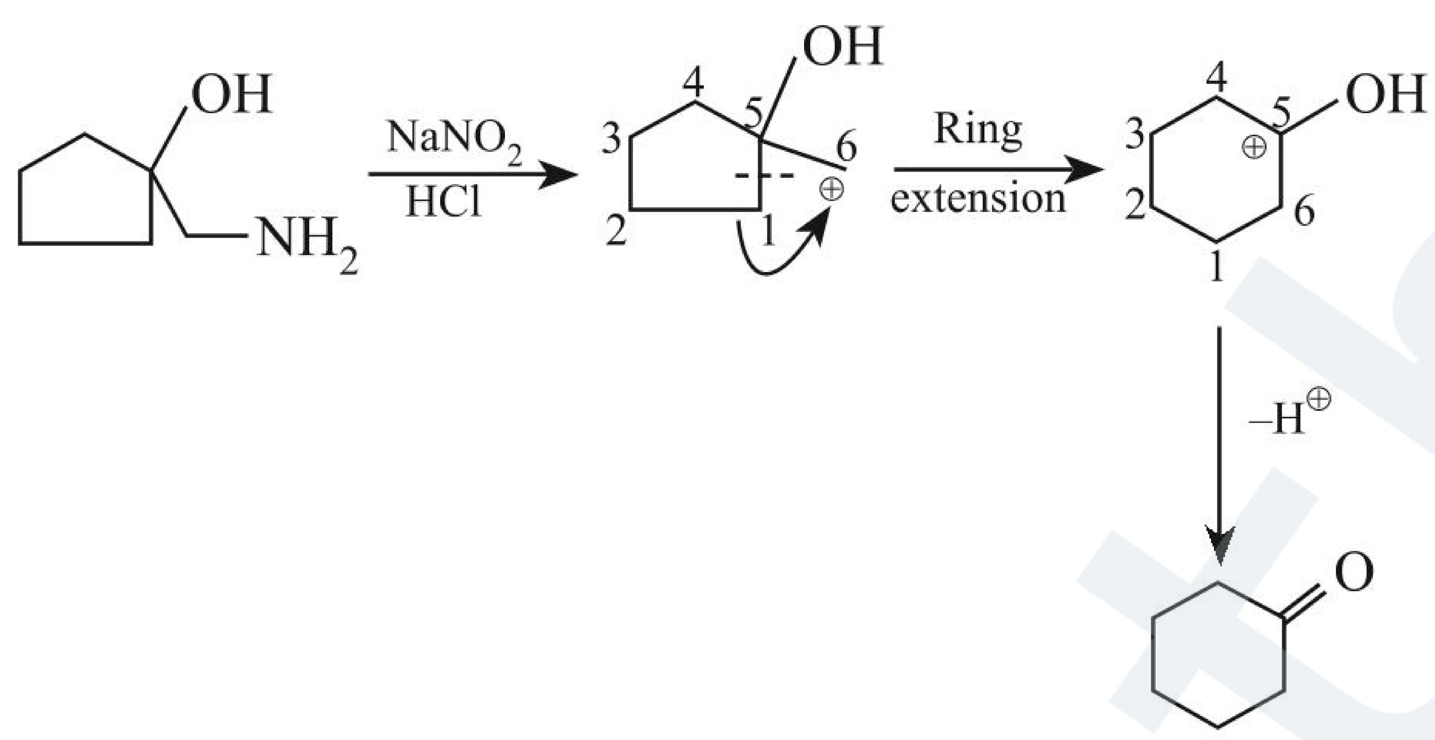


Products (B)

66. (1)

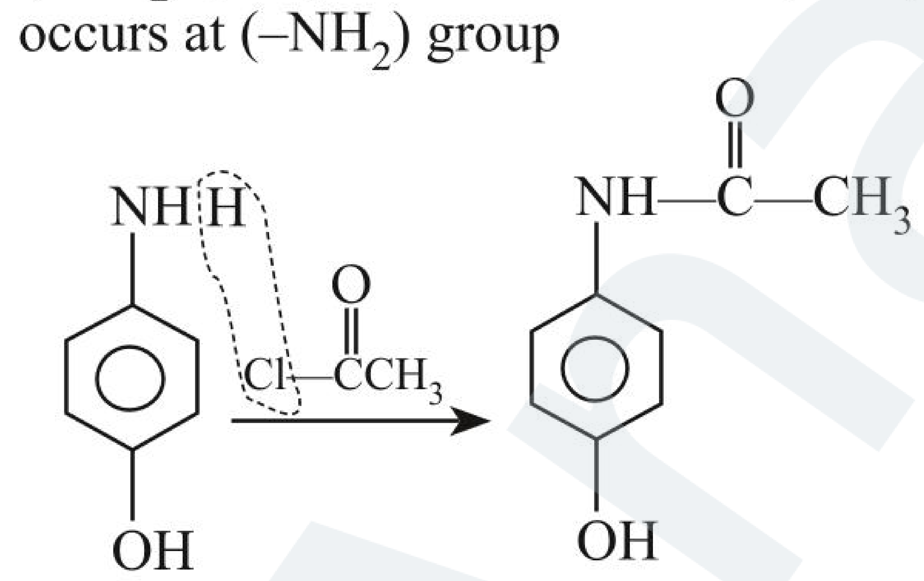


67. (3)



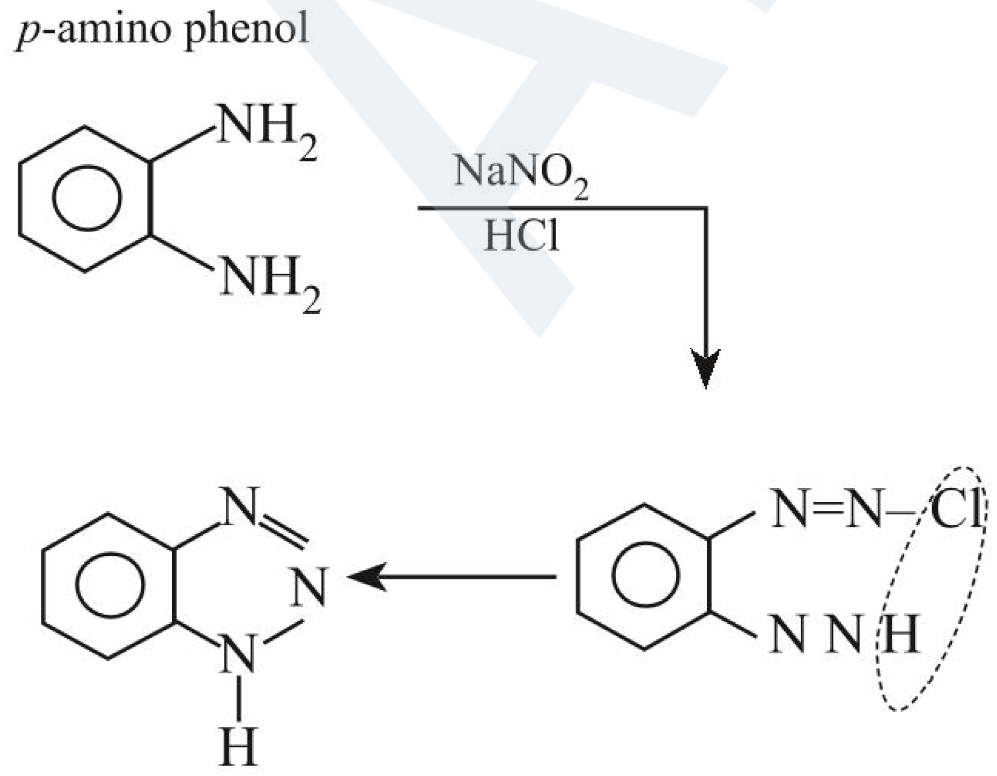
68. (2) III is stronger base due to lone pair of electrons on two N-atom. In I and II, lone pair of electrons are delocalised via resonance, thus weaker base than III. (IV) is stronger acid due to EW ($-SO_2$) group

69. (1) ($-NH_2$) group is more basic than ($-OH$) group, this acetylation occurs at ($-NH_2$) group



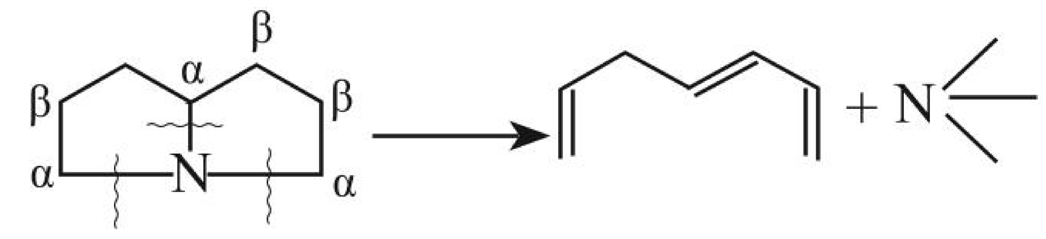
p-amino phenol

70. (2)

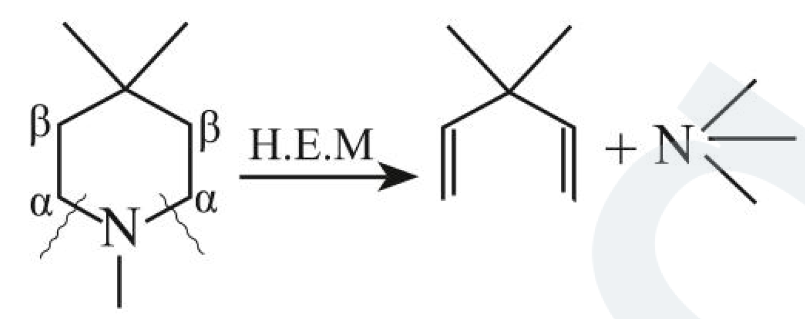


71. (2) Only in (2) lone pair of electrons on N atom are not in conjugation with double bond thus resonance does not occur, hence stronger base.

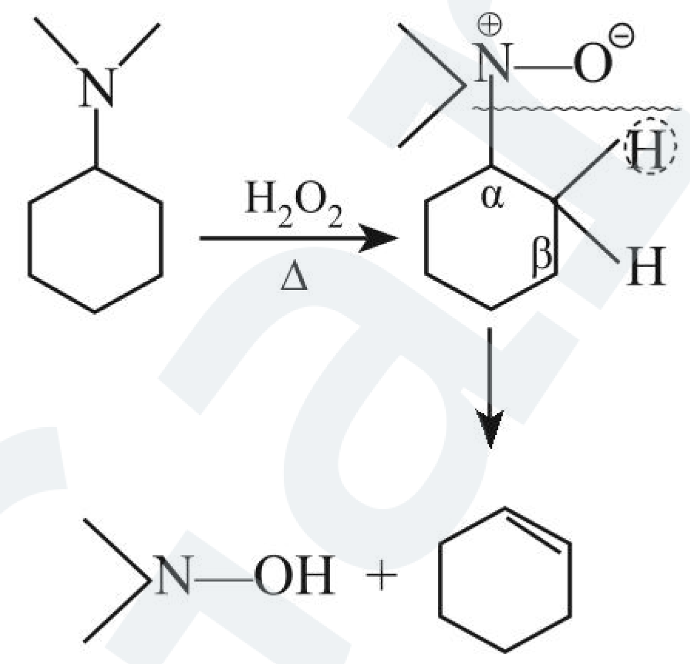
72. (4) It requires three Hoffmann sequences



73. (3) Hoffmann Elimination



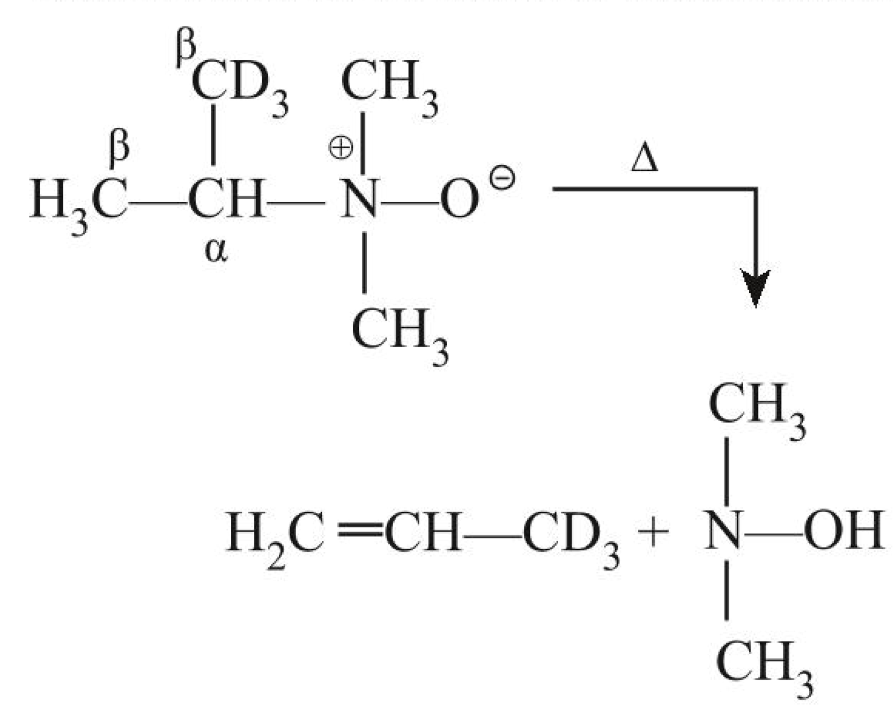
74. (3) It is Cope reaction



75. (2) Lithium salts are strongest base

76. (3) It is an example of Cope reaction.

Elimination of H-atom is faster and easier than D-atom.



77. (3) These facts are the properties of 2° amine.

78. (3) Since 1° aliphatic amines are more basic than 1° aromatic amine hence with 1 mole of HCl, salt is formed at 1° aliphatic amine

79. (3) Br-atom is more reactive than F-atom. So reaction occurs from Br-end (Refer to section 7.3.5).

80. (3) $PhN_2Cl \xrightarrow[KCN]{CuCN} Ph-C\equiv N$ (A)

$\xrightarrow{LAH}$ $PhCH_2NH_2$ (Benzyl amine) $\xrightarrow{HNO_2}$ $PhCH_2OH$ (Benzyl alcohol)

81. (2) More EWG in diazonium ion, faster it couples. more EDG in diazonium ion, less it couples ($-NO_2$) is EWG.

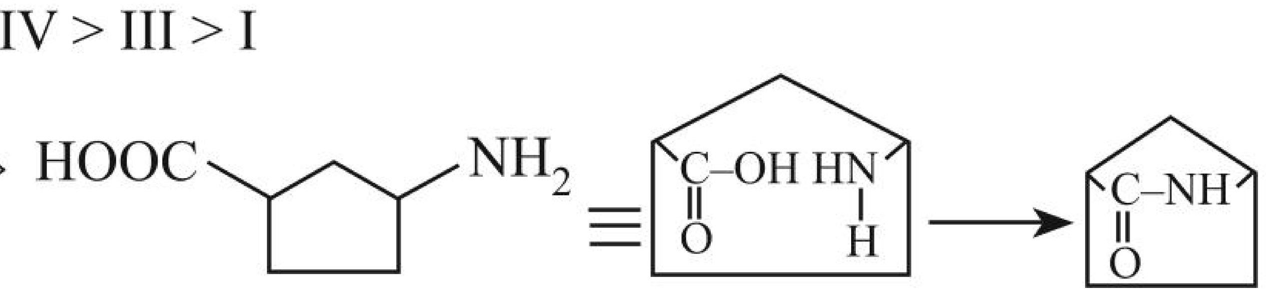
EDG order:

$(CH_3)_2\ddot{N}- > -OCH_3 > CH_3-$
(I) (II) (III)

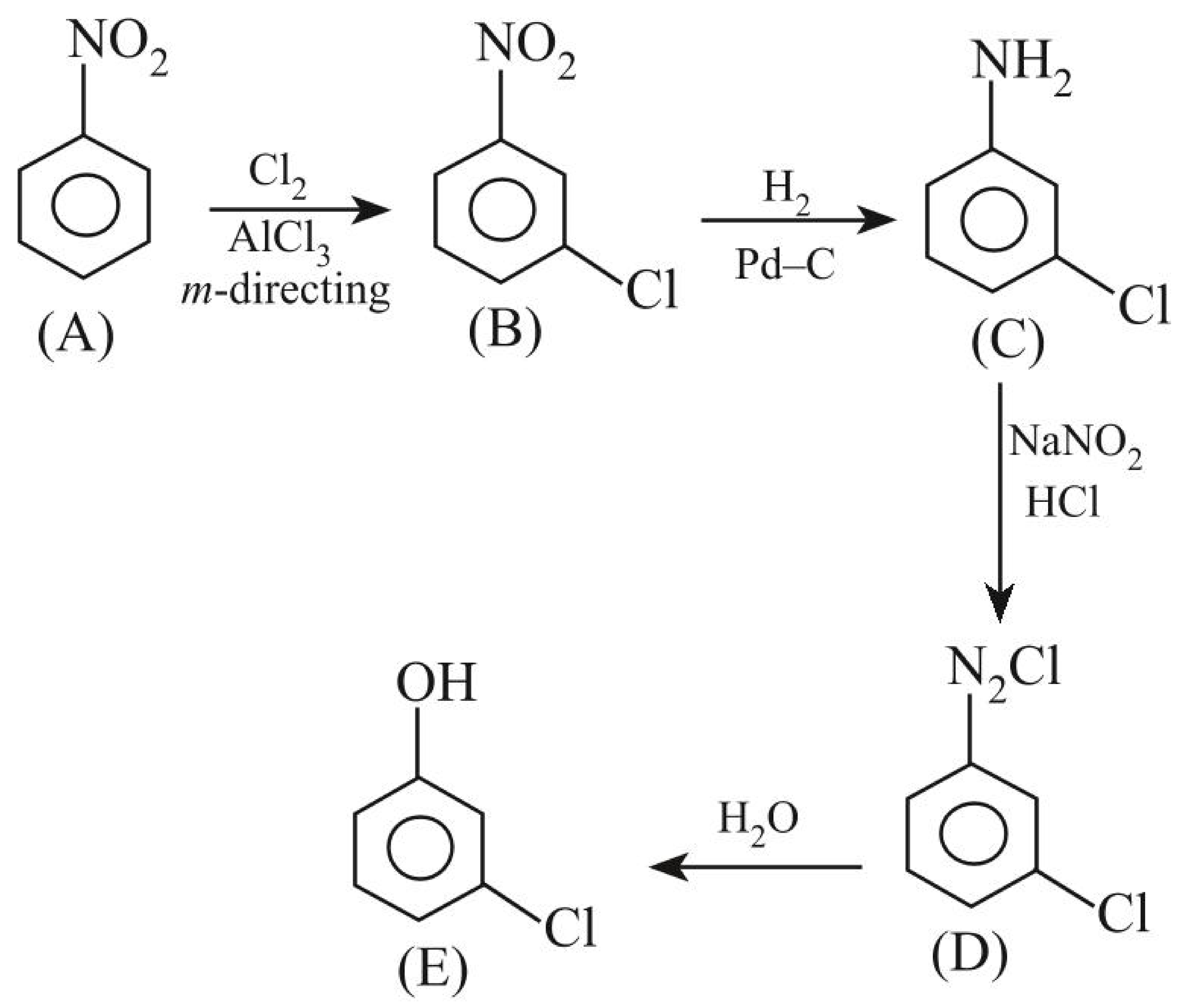
thus order of reactivity is :

II > IV > III > I

82. (2) A ⇒

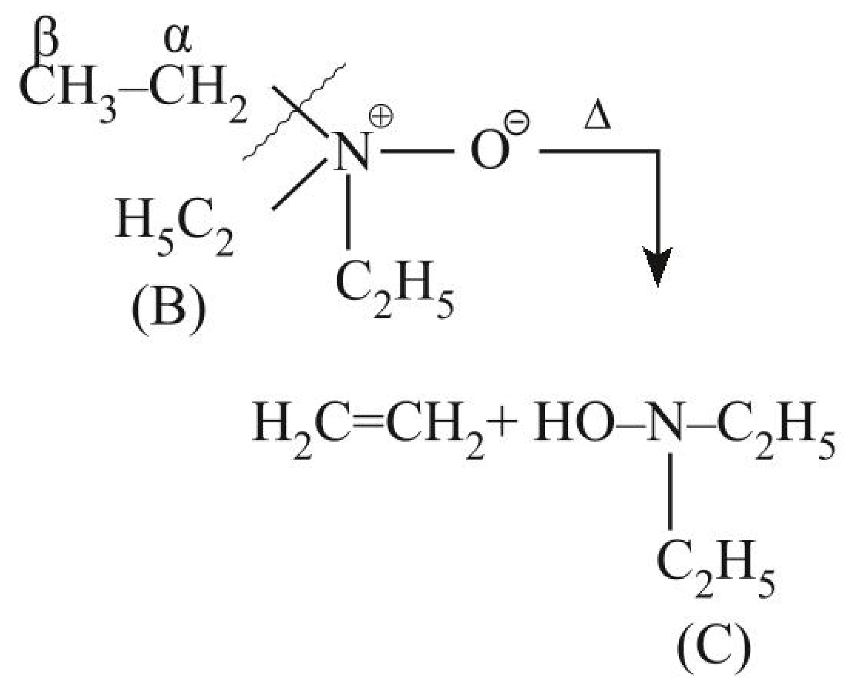


83. (3) N_2O_5 is nitrating reagent

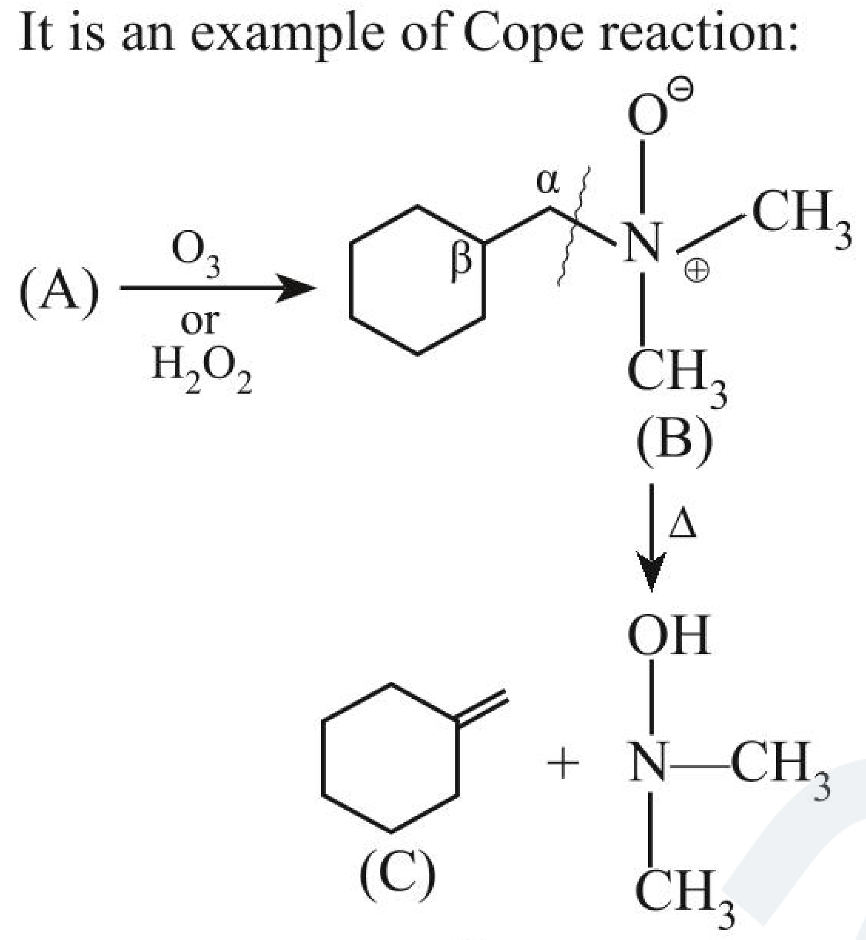


84. (2) $\underset{(B)}{C_2H_5COCl} \xrightarrow{NH_3} \underset{(C)}{C_2H_5CONH_2} \xrightarrow[\text{Hoffmann Bromamide}]{KOH + Br_2} \underset{(D)}{C_2H_5NH_2}$

85. (4) It is a Cope reaction



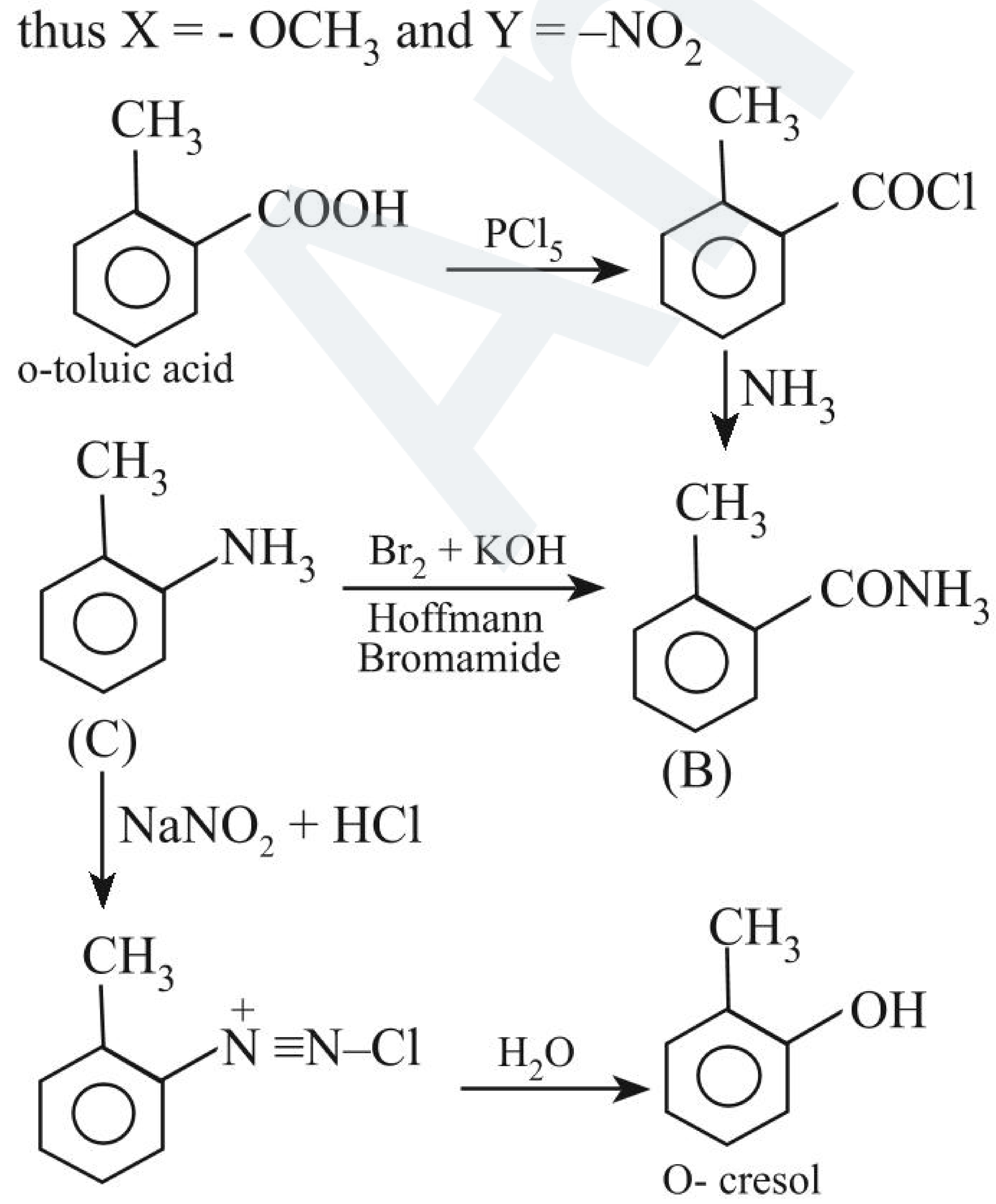
86. (1) It is an example of Cope reaction:



87. (1) For coupling $PhN_2^{\oplus}$ must have EWG and coupling reagent must have EDG.

thus X = - OCH_3 and Y = $-NO_2$

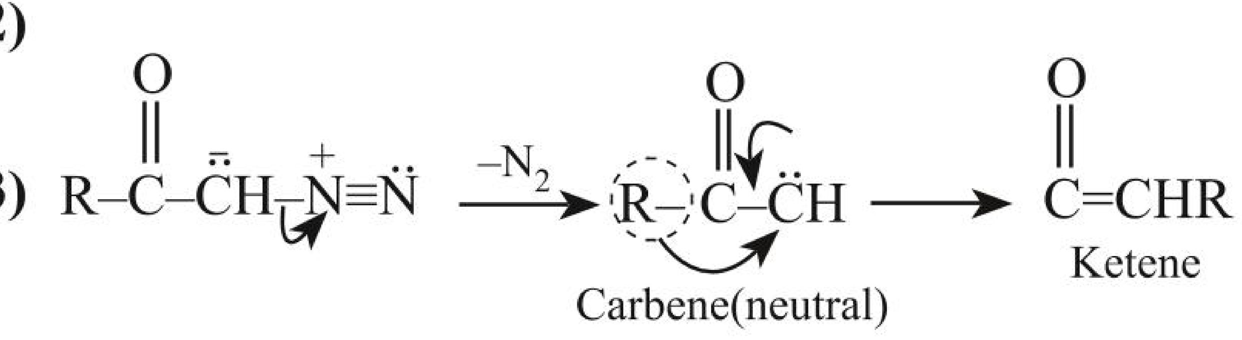
88. (4)



89. (3) Refer to section 7.10

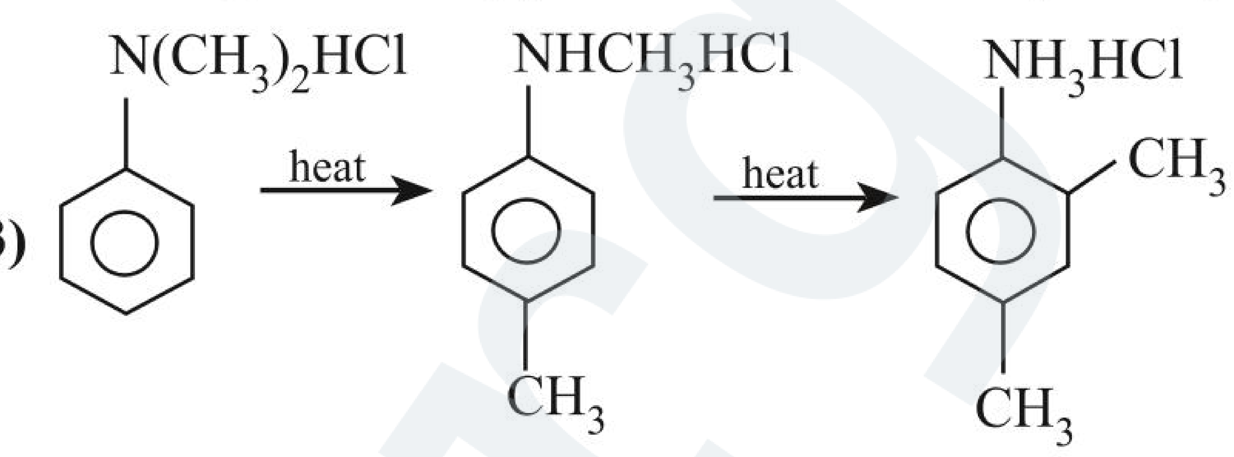
90. (2)

91. (3)

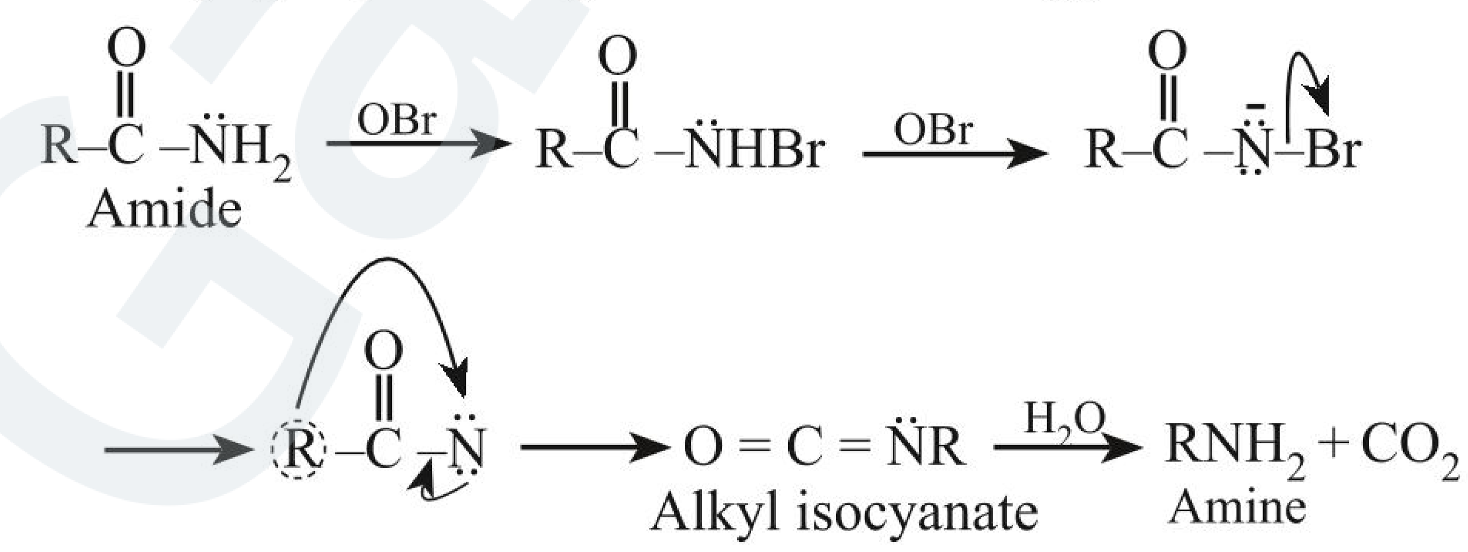


92. (3) Nitro compounds, being relatively more polar than nitrites, have higher boiling points than the corresponding nitrites.

93. (3)



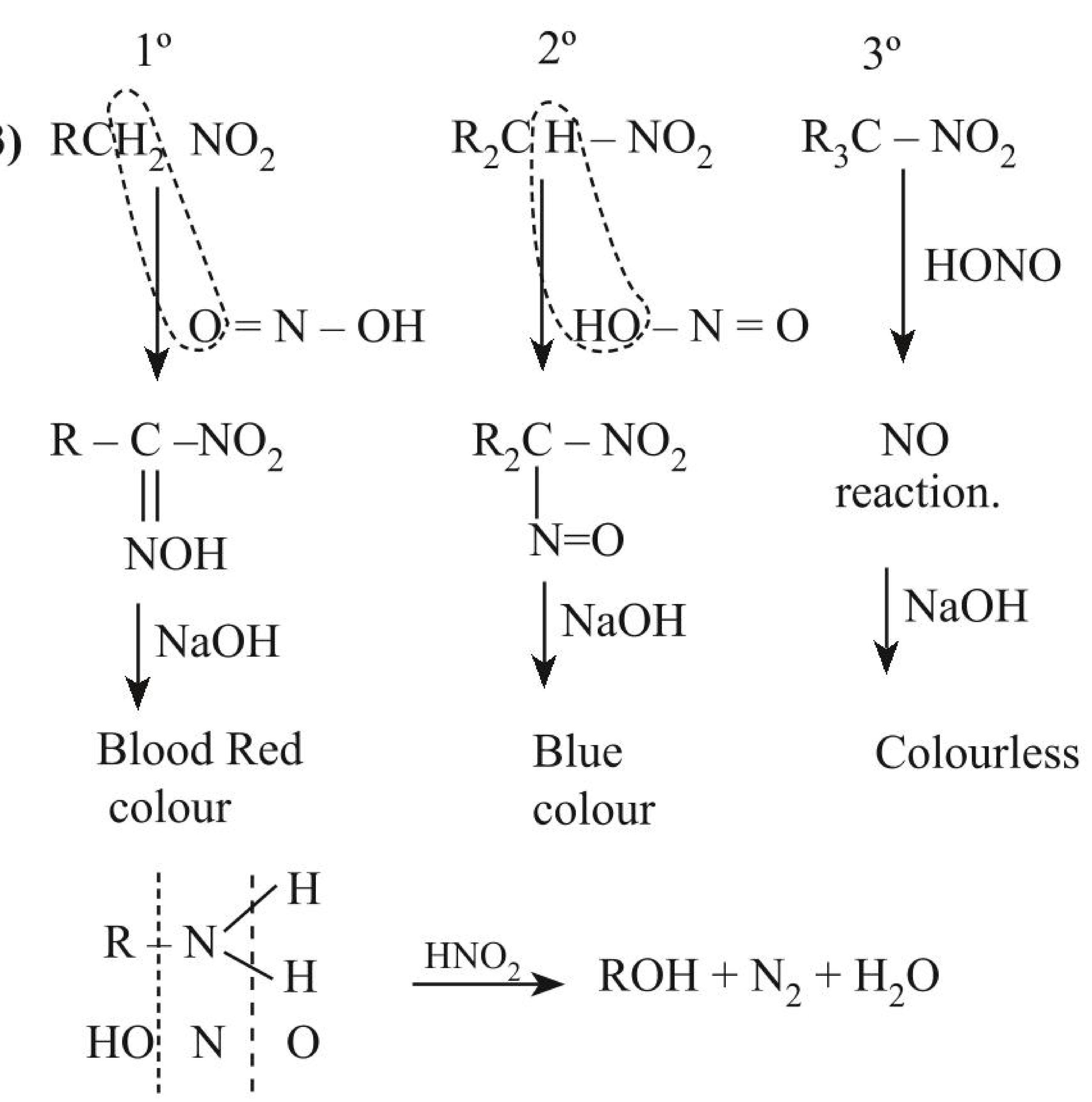
94. (4) For this one should remember that Hoffmann's degradation involves migration to electron deficient nitrogen atom, hence the alkyl group will migrate with its bonding pair of electrons.



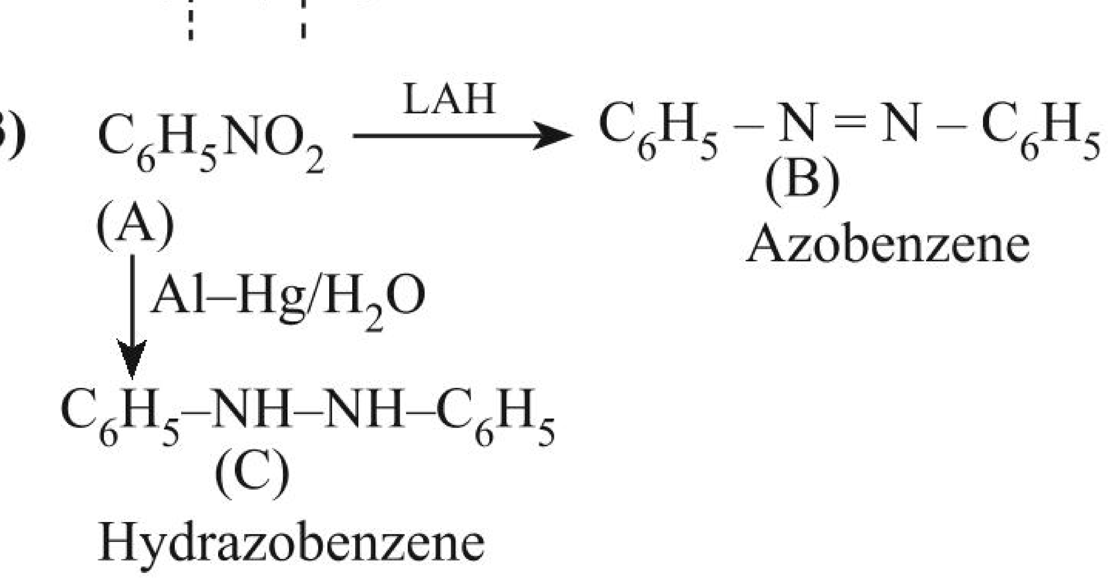
(Note that N is electron deficient.)

95. (2) $\underset{(A)}{C_2H_5Cl} \xrightarrow{AgCN} \underset{(B)}{C_2H_5Cl} \xrightarrow[\text{CH}_3\text{SOCH}_3\ (\text{DMSO})]{Cl_2 +} C_2H_5NCO + CH_3S(Cl_2)CH_3$

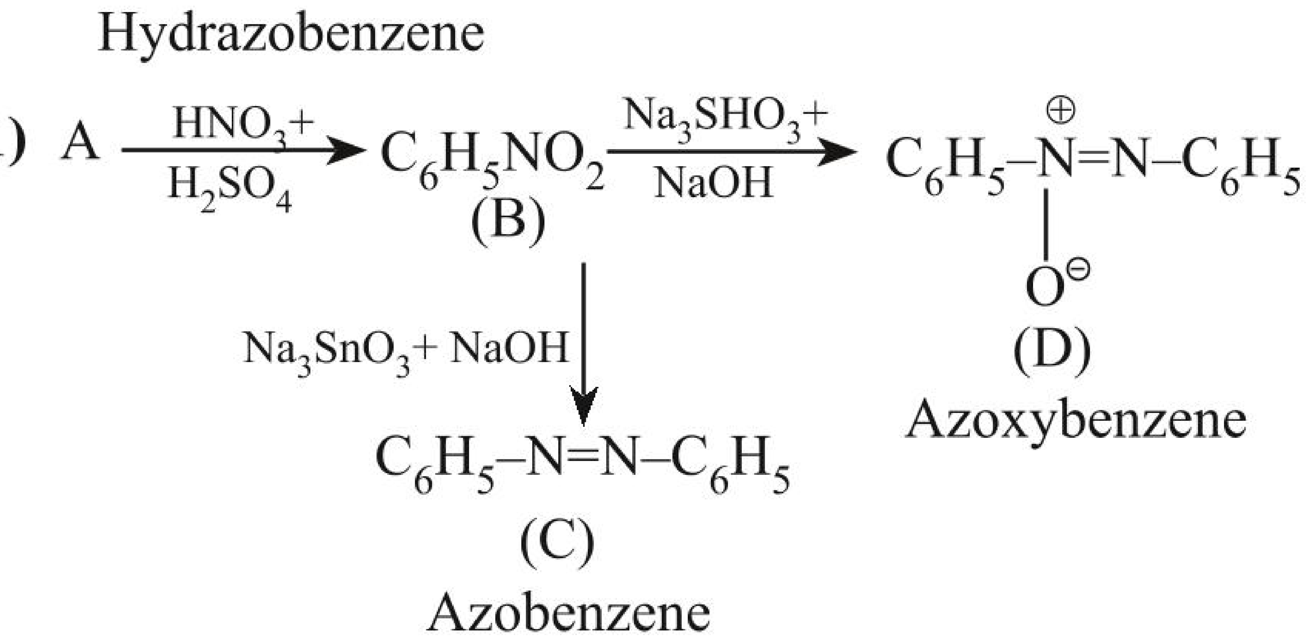
96. (3)



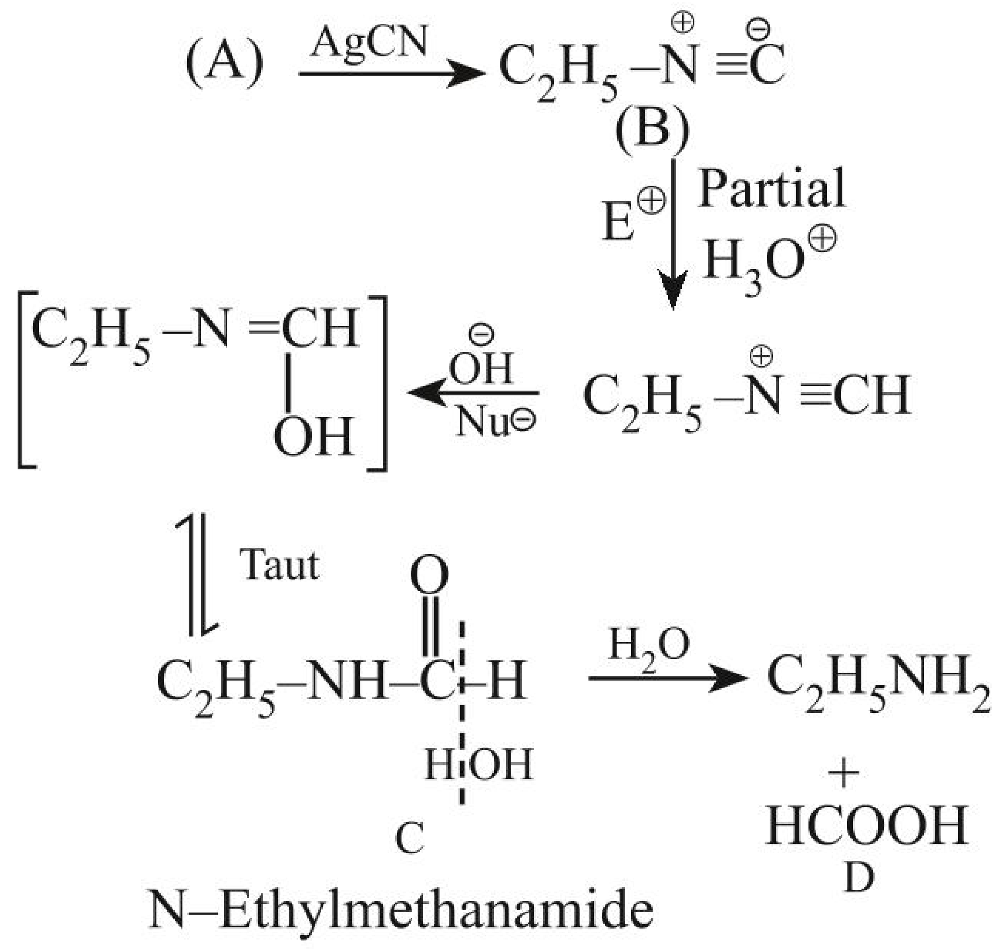
97. (3)



98. (1)



99. (1)



100. (3) Evolution of N_2 with HNO_2 suggests that 1° amine [either (a) or (c)]. 59.07 gm of (I) is present in 100 gm of compound.

127 gm of I (1mol) in present in $\dfrac{100 \times 127}{59.07} = 215$

Molecular mass = 215

(1) $CH_3NH_2 \xrightarrow{3CH_3I} \left[CH_3—\overset{\oplus}{N}(CH_3)_3\right]I^{\ominus}$

(Molecular mass = 201)

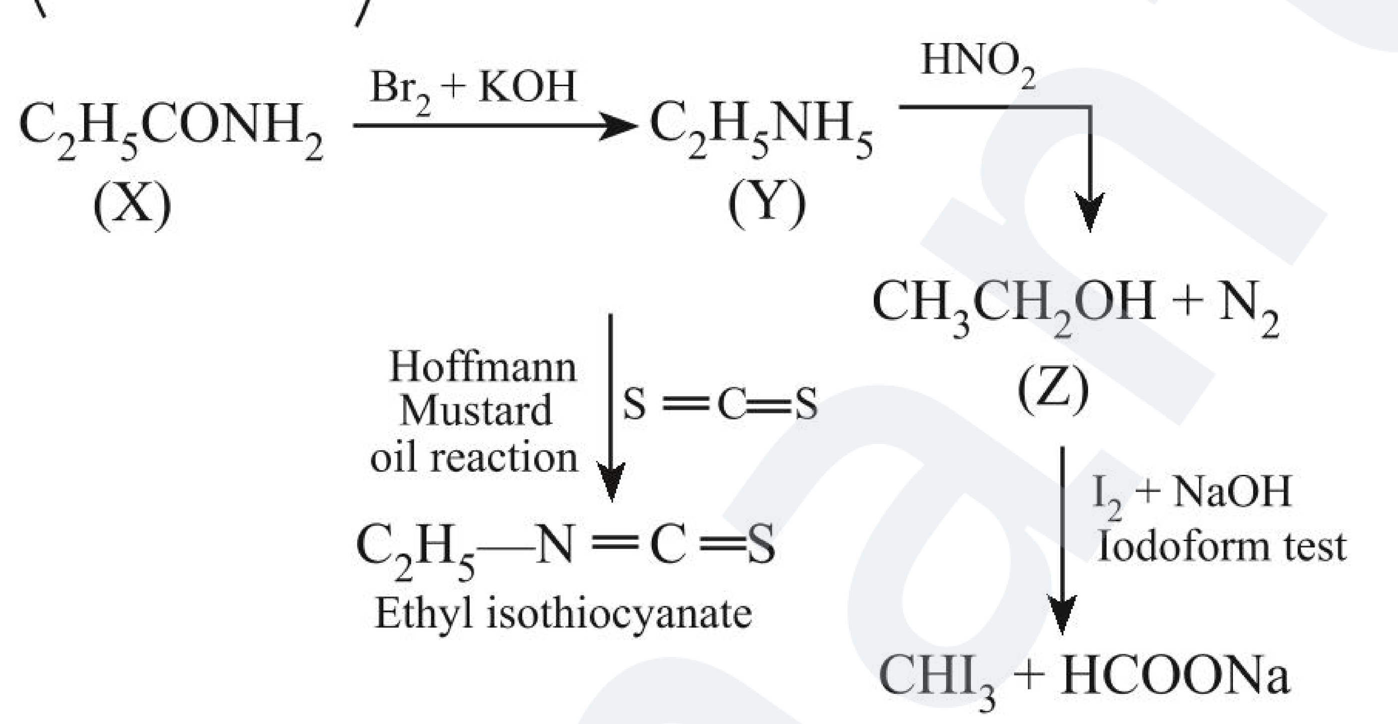
(2) $C_2H_5NH_2 \xrightarrow{3CH_3I} \left[C_2H_5—\overset{\oplus}{N}(CH_3)_3\right]I^{\ominus}$

(Molecular mass = 215)

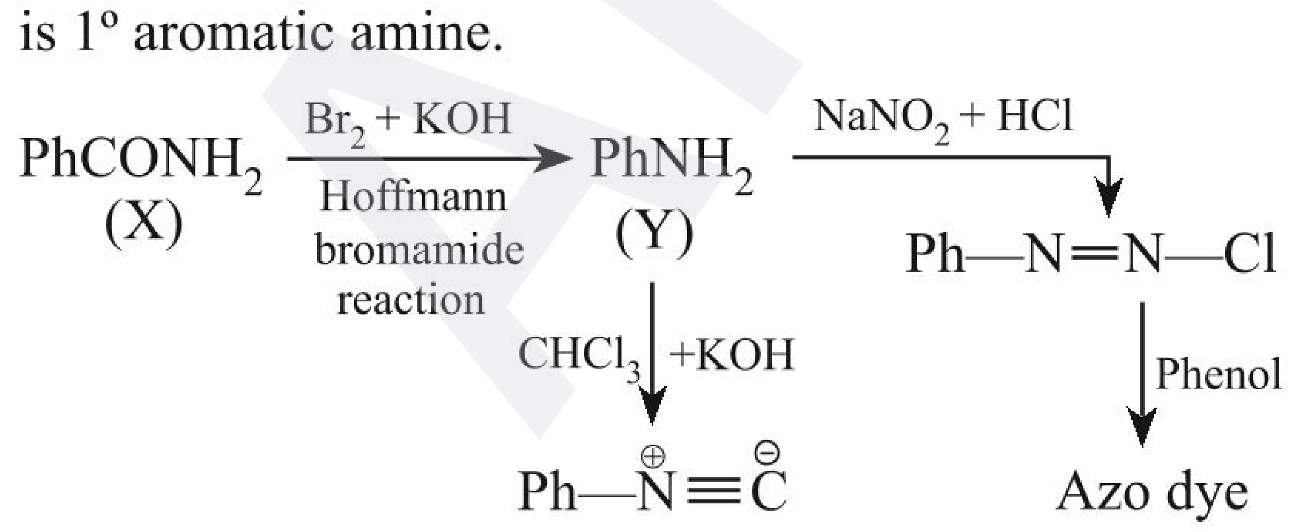
Hence, the amine is $C_2H_5NH_2$

101. (1) Reaction of (X) with Br_2 + KOH suggests that (X) is an amide. Evolution of N_2 and formation of alcohol suggest that (Y) is a 1° aliphatic amine. Iodoform test of (Z). It suggests that it is an alcohol of the Type

$\left(CH_3—\underset{OH}{CH}—\right)$



102. (1) Reaction of (X) with Br_2 + KOH suggests that (X) is an amide. Carbylamine test and coupling reaction of (Y) suggest that (Y) is 1° aromatic amine.



103. (2) $C_2H_5\overset{O}{\overset{\|}{C}}—NH_2 \xrightarrow[-H_2O]{P_2O_5} C_2H_5—C\equiv N$ Ethanenitrile

104. (1) $Me—C\equiv N + MeMgBr \xrightarrow[H_2O]{} Me—\overset{O}{\overset{\|}{C}}—Me$ Propanone

105. (1) $C_2H_5OH + Me—C\equiv N \xrightarrow{H_2SO_4}$

$C_2H_5—O—\overset{O}{\overset{\|}{C}}—Me \leftarrow C_2H_5OH + HO—\overset{O}{\overset{\|}{C}}—Me$

Ethyl acetate

Me—C……N is hydrolysed to acid which reacts with alcohol to give ester.

106. (2) $PhNH_2$ (Benzenamine) + $CHCl_3$ (Trichloro methane) + 3NaOH $\xrightarrow{\text{Carbylamine reaction}}$ $Ph—\overset{\oplus}{N}\equiv \overset{\ominus}{C} + 3NaCl + 3H_2O$ (Phenylisocyanide)

107. (4) Reduction with Zn–Hg/HCl is Clemmensen reduction which converts $\left(\rangle C=O \rightarrow CH_2\right)$, $(R—C……N \rightarrow RCH_2NH_2)$, and $\left(R—\overset{\oplus}{N}\equiv\overset{\ominus}{C} \rightarrow RNHCH_3\right)$.

Carbylamino methane is $\left(Me—\overset{\oplus}{N}\equiv\overset{\ominus}{C}\right)$.

$\therefore Me—\overset{\oplus}{N}\equiv\overset{\ominus}{C} \xrightarrow{Zn–Hg/HCl} Me—NH—CH_3$ *N*-Methylmethanamine

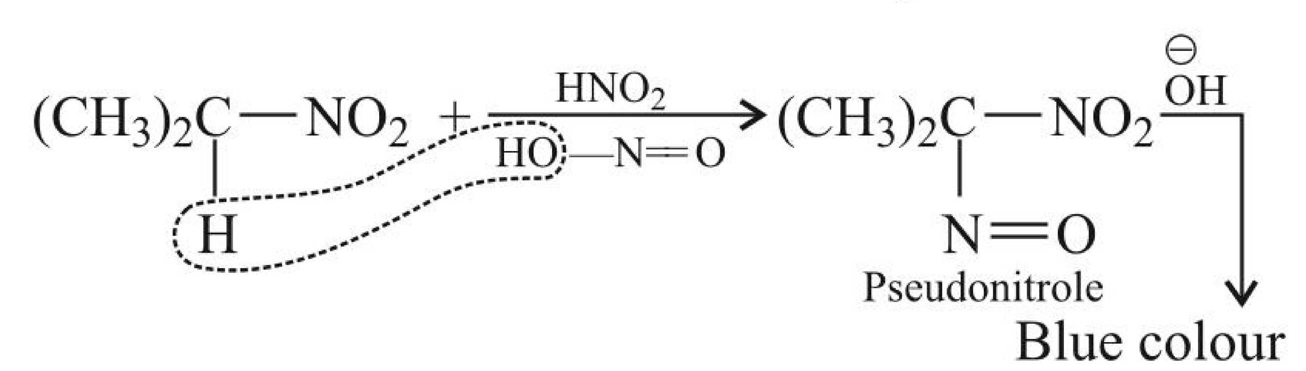
108. (4) $CH_3CH_2CH_3 \xrightarrow{\text{Fuming } HNO_3}$ $CH_3CH_2NO_2 + CH_3\underset{NO_2}{CH}CH_3 + C_2H_5NO_2 + MeNO_2$

109. (3) $PhNO_2 \xrightarrow{Zn + NH_4Cl} PhNHOH$ *N*-Phenyl hydroxylamine

110. (2) $RCH_2NO_2 \xrightarrow[O=N—OH]{HNO_2} R—\underset{N—OH}{\underset{\|}{C}}—NO_2$ Nitrolic acid

111. (3) $H_3C—NO_2 \xrightarrow{Cl_2 + NaOH} Cl_3C—NO_2$ Chloropicrin (tear gas)

112. (4) The reaction is a test for 2° nitro compound.



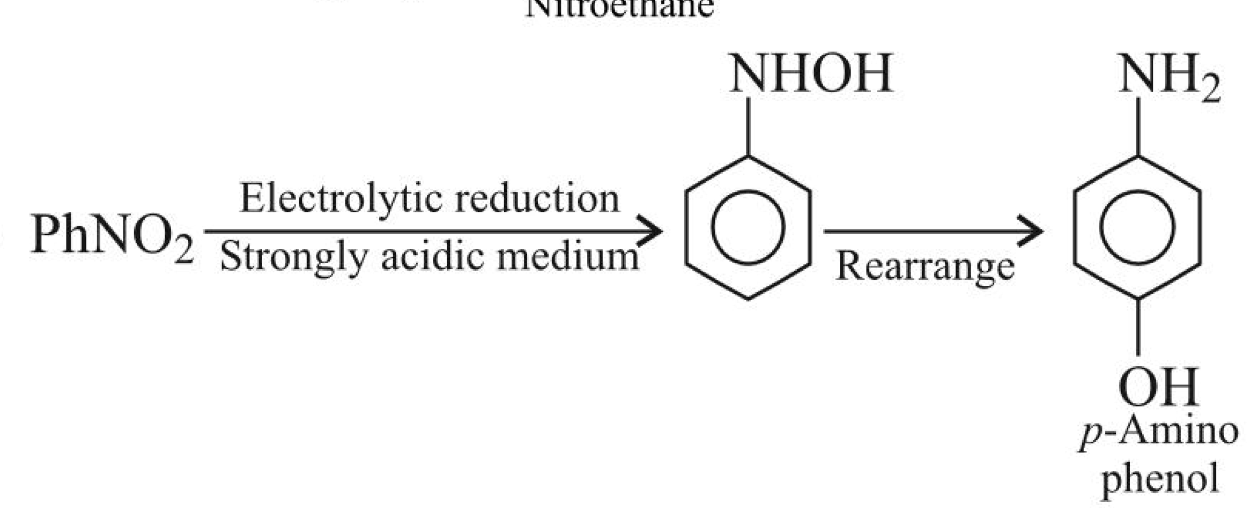
113. (2) Isocyanides on hydrolysis give 1° amine and HCOOH. Formic acid reduces Fehling's solution.

$C_2H_5—N\equiv C \xrightarrow{H_2O} C_2H_5NH_2 + HCOOH$

114. (2)

115. (3) $C_2H_5Br \xrightarrow[AgNO_2]{alc.} C_2H_5NO_2$ Nitroethane

116. (2)



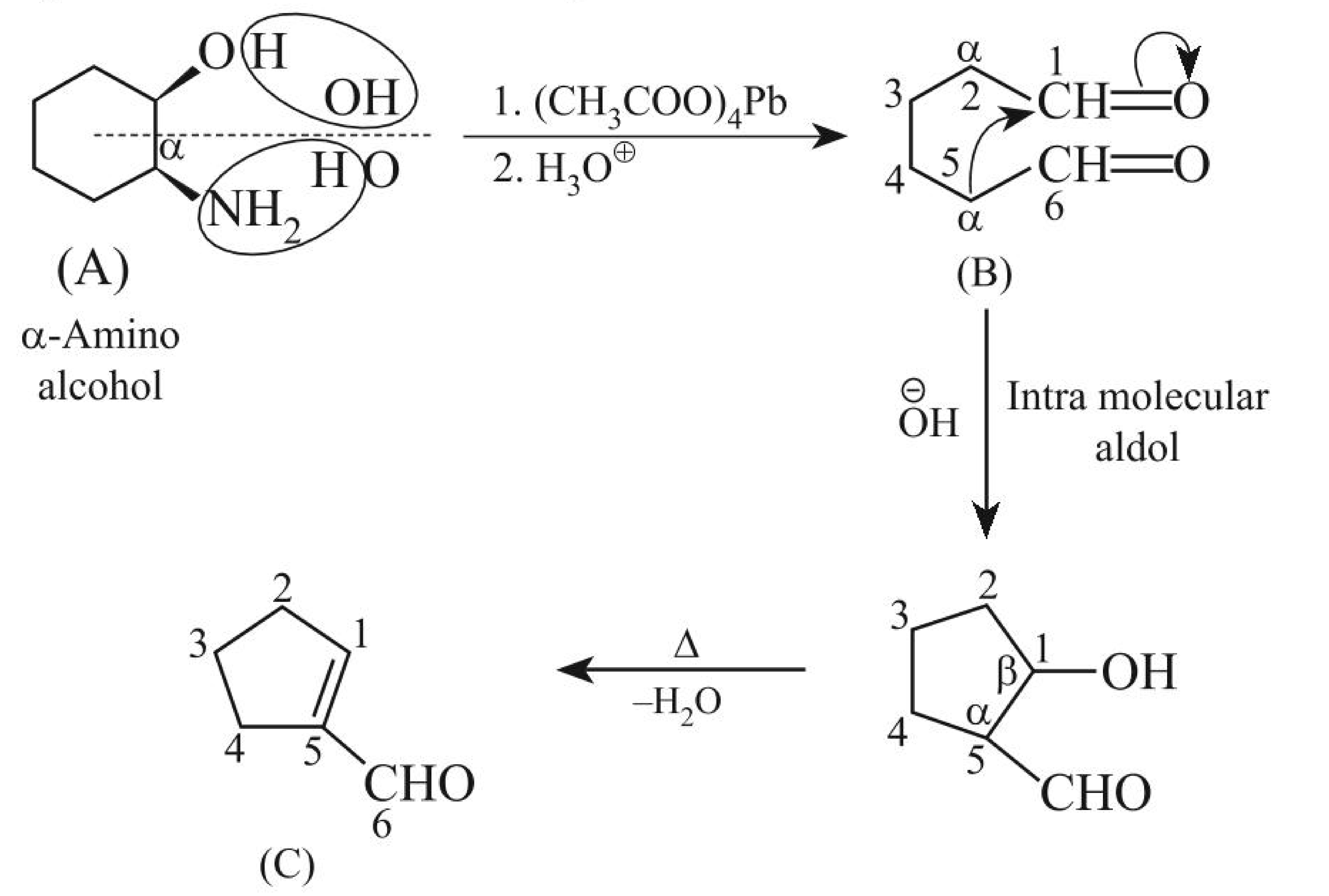
117. (3)

118. (3) Nitroalkane containing α-H atoms, i.e., 1° and 2° nitro alkanes show tautomerism.

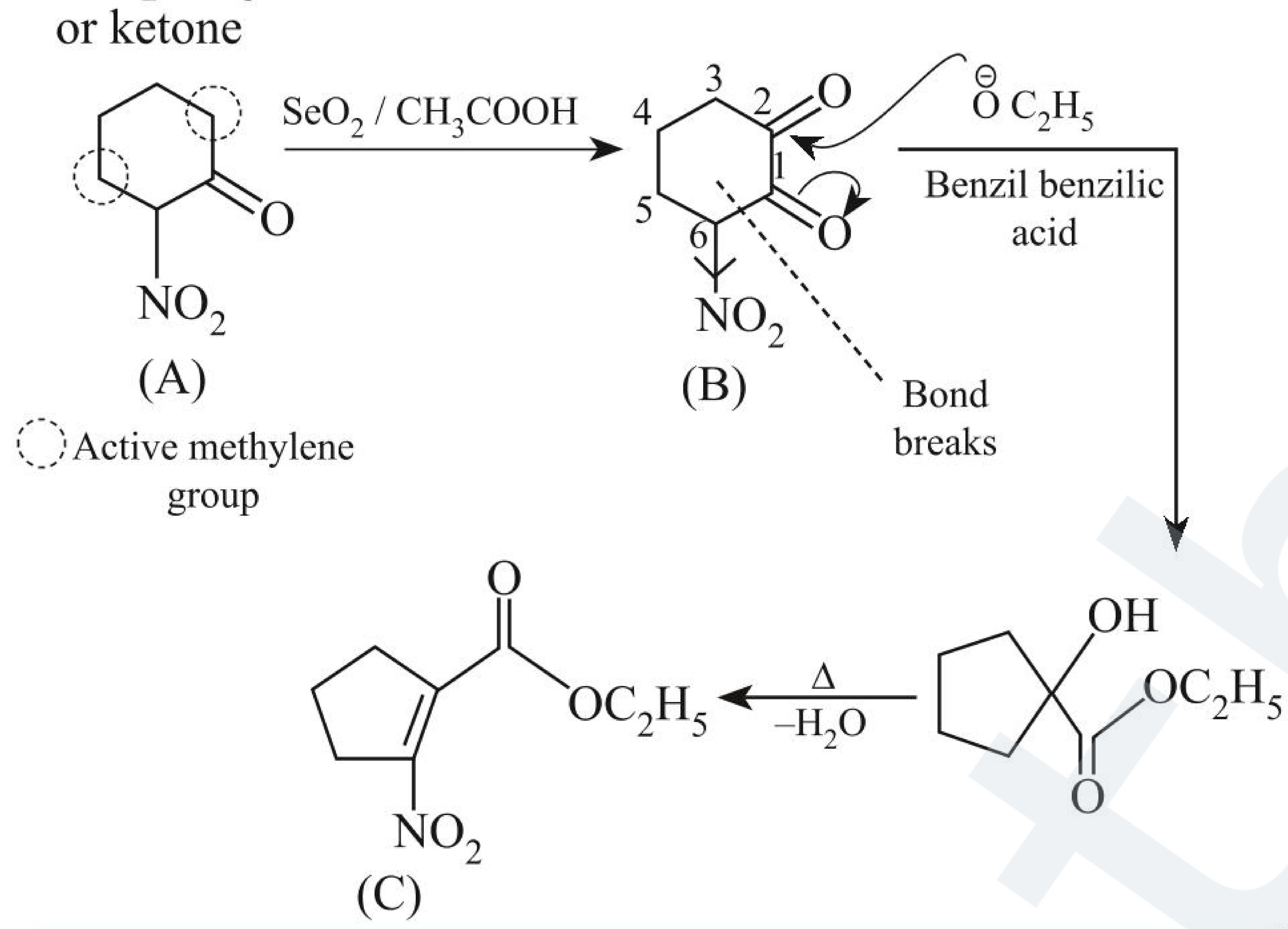
119. (4)

120. (1)

121. (4) With HIO_4 or $(CH_3COO)_4Pb$ or sodium bismuthate the cleavage of adjacent (–OH) and ($–NH_2$) or α-amino alcohol takes place to give aldehyde or ketone or acids depending upon the structure of compound.

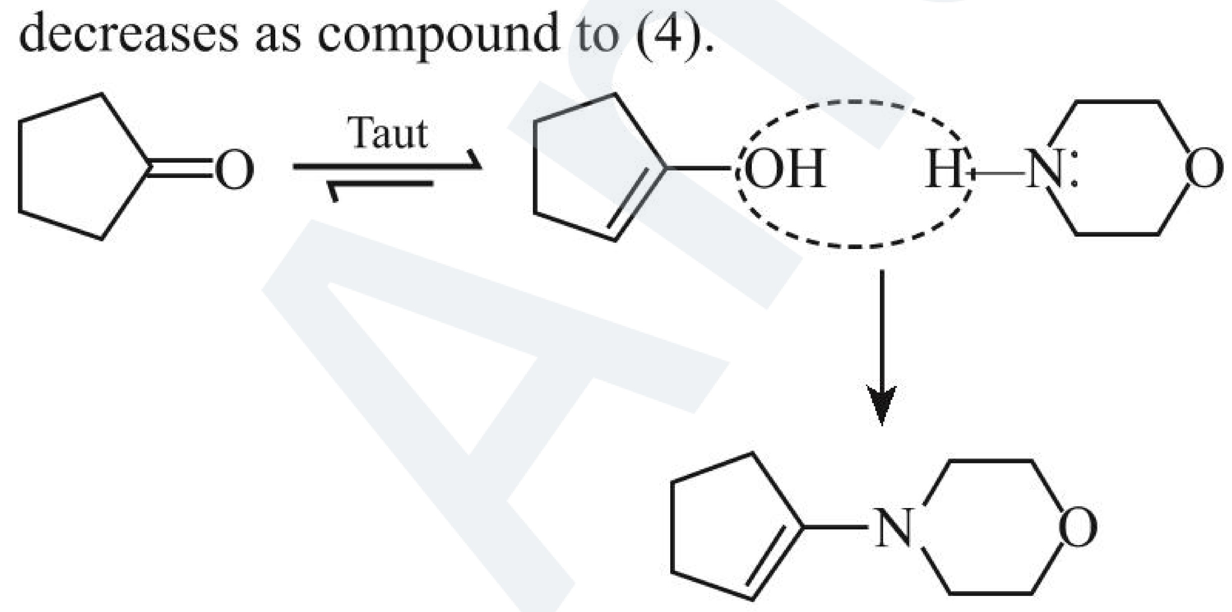


122. (3) SeO_2/CH_3COOH oxidises active methylene group to aldehyde or ketone



Note: Out of two (C=O) group, NA. reaction with $C_2H_5O^{\ominus}$ will take place on the more reactive (C=O) group, containing EWG ($—NO_2$), Thus the same C^6-atom will migrate to other (C=O) group, giving α-hydroxy acid.

123. (4) It is an example of Stork Enamine reaction 2° amine, react with carbonyl compounds with at least one α-H-atom and form enamine. (c) and (d) both are 2° amine but in (c), lone pair $\bar{e}$'s on N-atom are delocalised by resonance (LP $\bar{e}$'s are in conjugation with (C=O) group). Hence in (3), basic character decreases as compound to (4).



Enamine

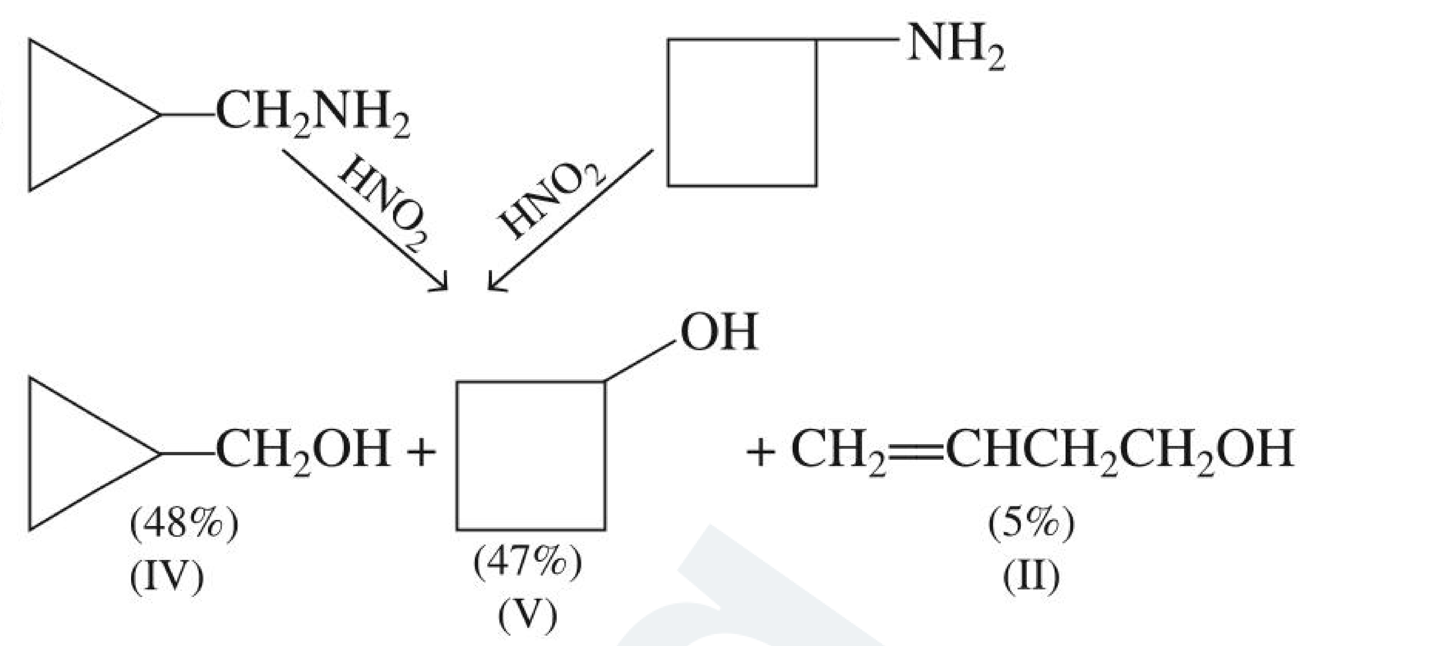
124. (4) Bronsted acid is weaker base.

(II) is strongest Bronsted acid but weaker Bronsted base, since LP $\bar{e}$'s on N-atom are delocalised *via* resonacne (because LP $\bar{e}$'s on N-atom are in conjugation with (C=O) group).

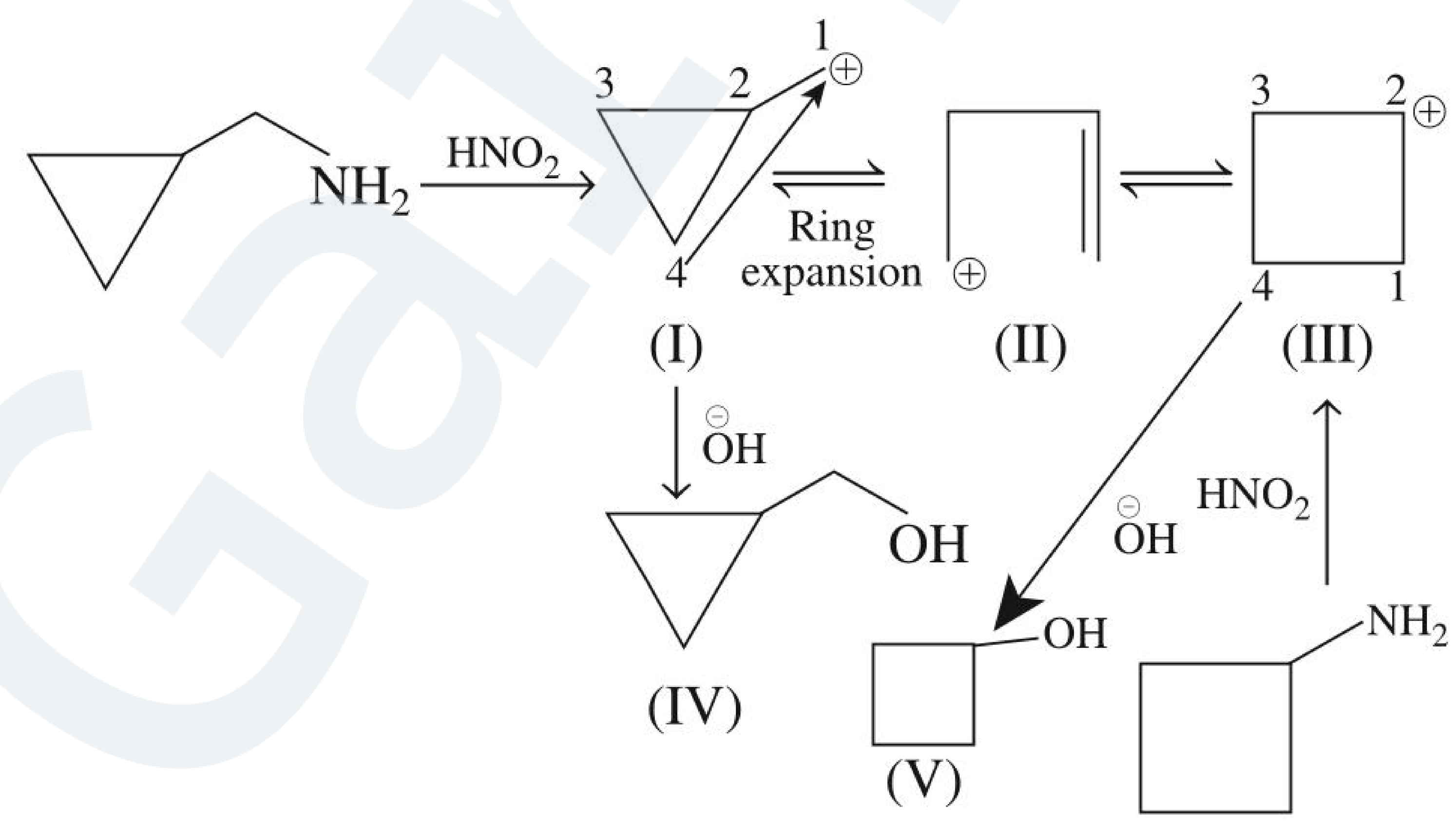
Alternatively; due to EWG (C=O) II is weakest base and strongest Bronsted acid.

(IV) Strongest base ue to 3 LP $\bar{e}$'s on 3 N-atoms. Only 2 LP $\bar{e}$'s on 2 N-atom are in conjugation.

125. (2)

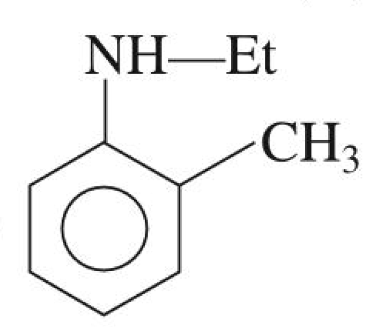


The reaction proceeds through common intermediates and can be explained on the basis that the ion formed from each substrate equilibrates rapidly with other structures through which the same mixture of products is formed, e.g.,



From the analysis of the products, it would appear that (I) and (III) have about the same stability, both being much more stable than (II).

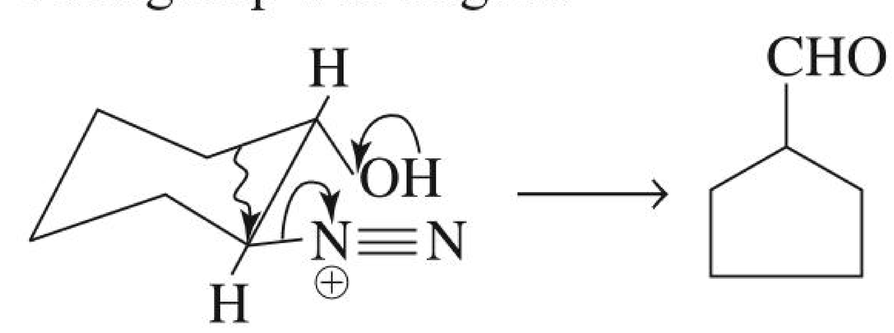
126. (4)



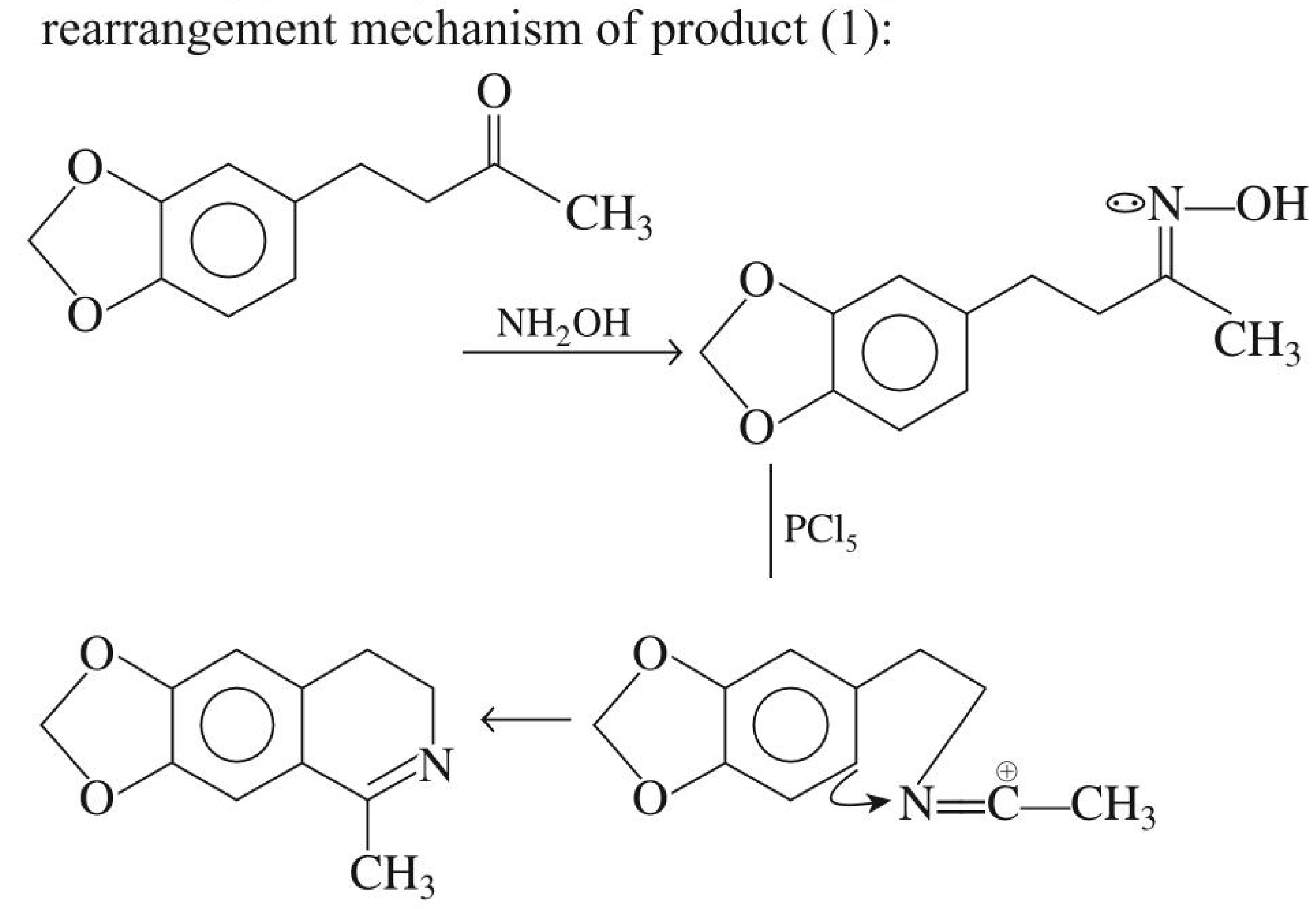
(2° amine will not form diazonium salt.)

127. (3) Solvation of nucleophile is very less in presence of quartenary ammonium salt.

128. (3) Anti group will migrate

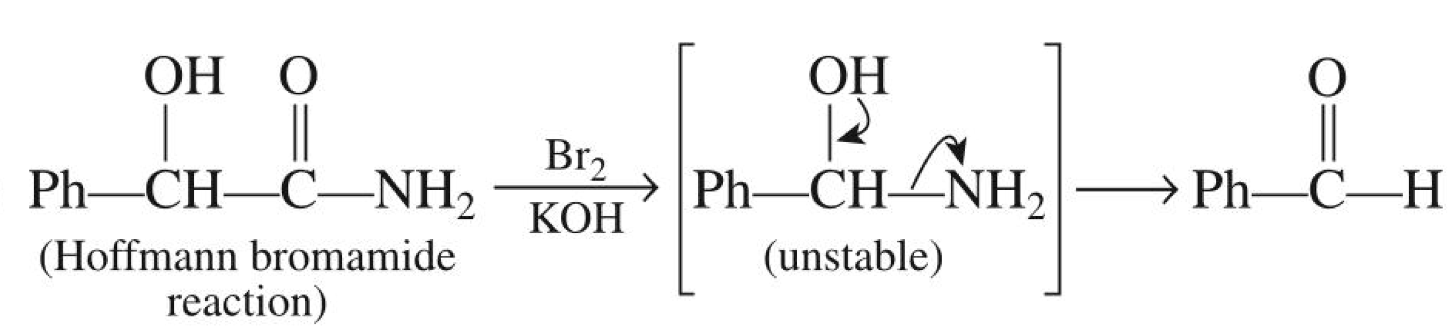


129. (4) Product (2) and (3) will be obtained by normal Backmann rearrangement mechanism of product (1):



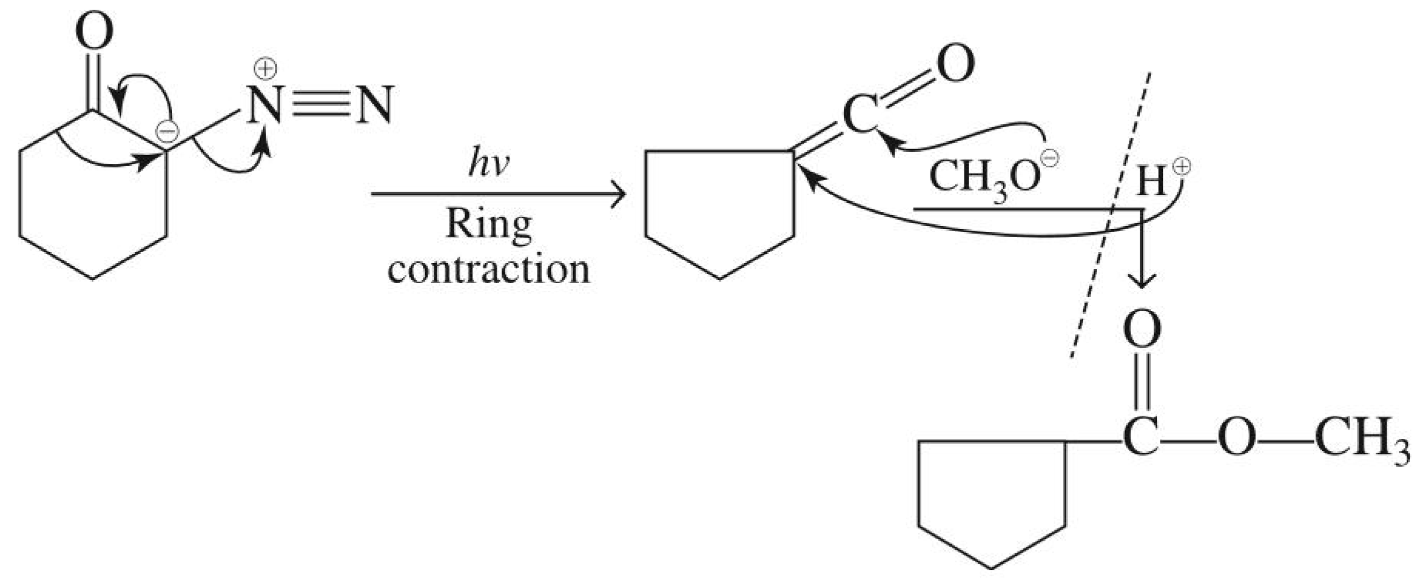
(electrophilic aromatic substitution)

130. (2)

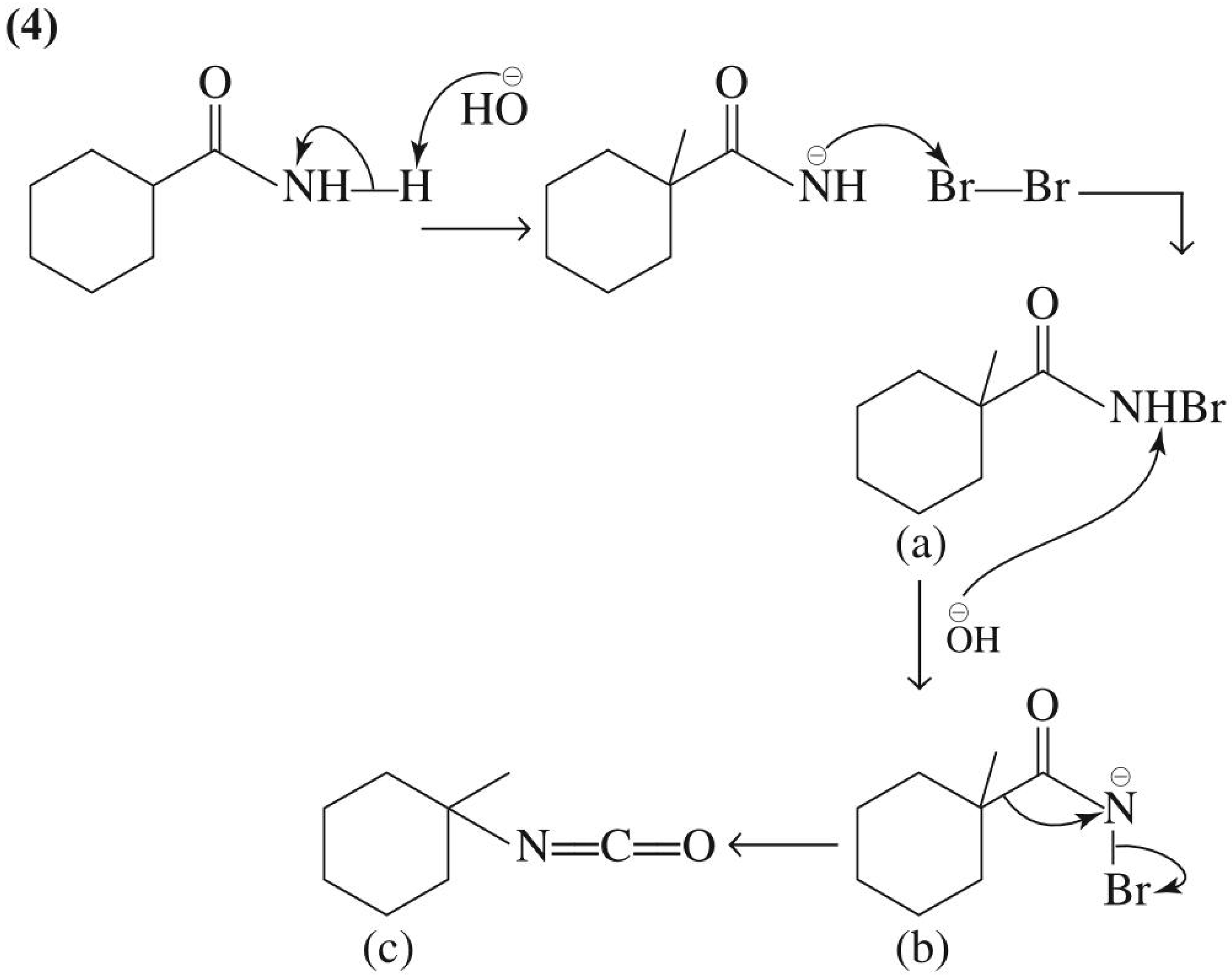


131. (3) Simmon-Smith reaction.
Carbene insertion at all the three double bonds.

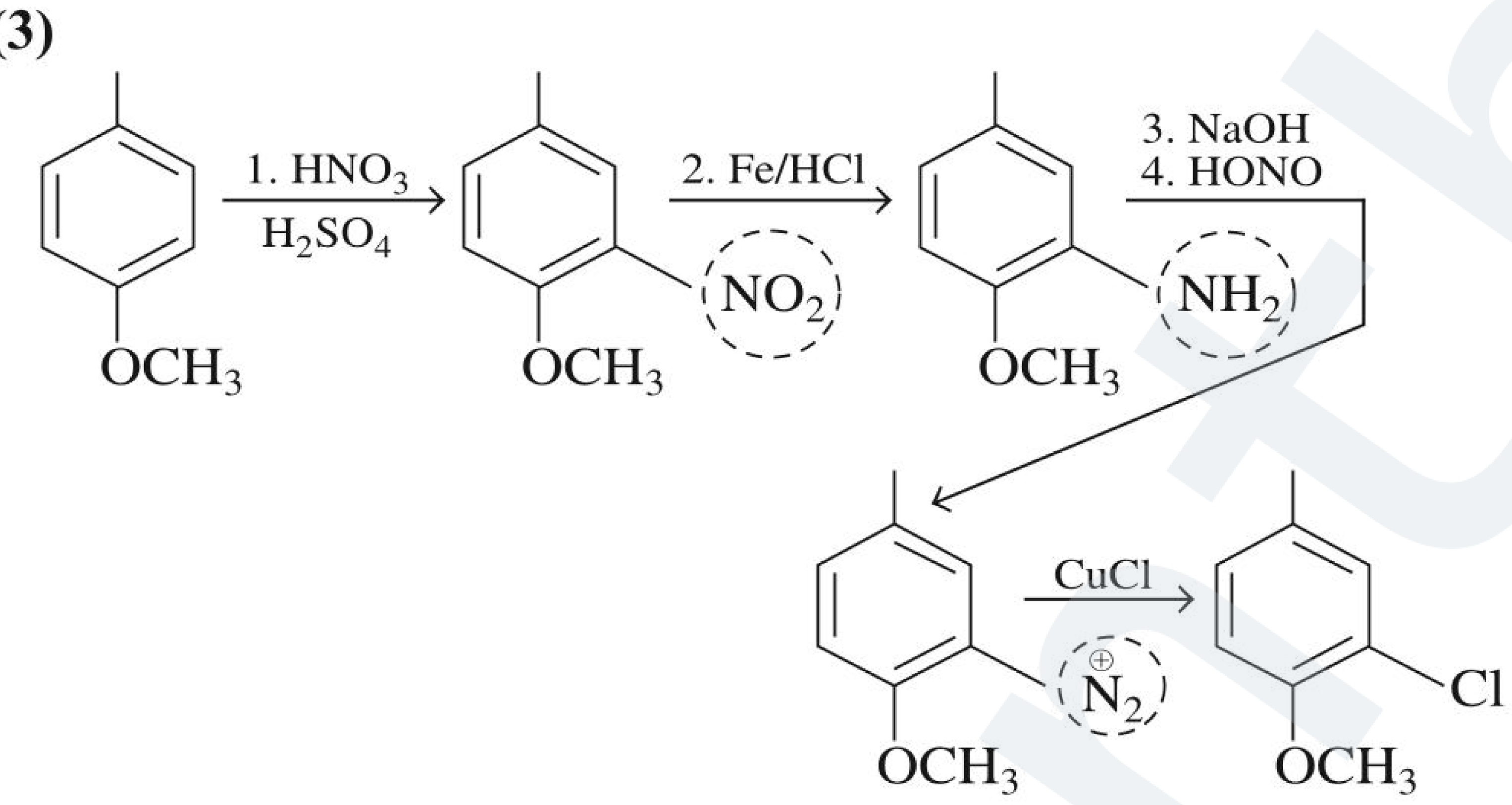
132. (1)



133. (4)

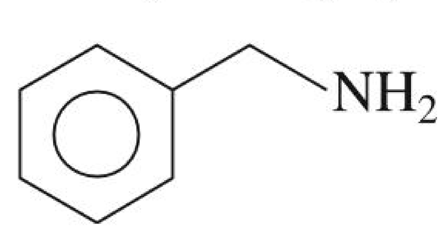


134. (3)



135. (2) CH_3NH_2, $CH_3CH_2NH_2$
(A) (B)

136. (4) $POCl_3$ and P_2O_5 act as dehydrating agents.

137. (2)  is protonated in acidic medium.

138. (3) Only 1°-amide gives H.B. Reaction.

139. (2) $CH_3CONH_2 \longrightarrow \underset{(A)}{CH_3NH_2} \xrightarrow[\text{D from solvent}]{D_2O} CH_3ND_2$

140. (1) H.B. degradation occurs with retention of configuration of chiral centre.

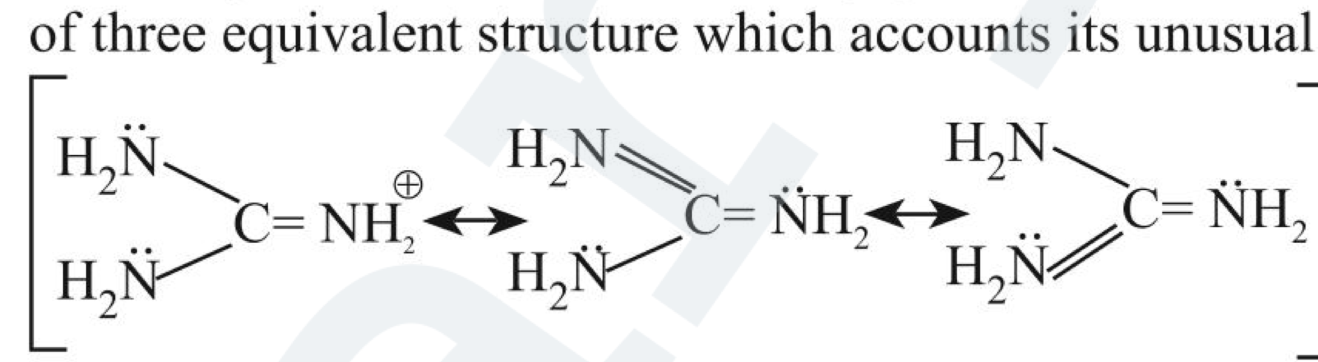
Multiple Correct Answers Type

1. (1, 2, 3)
(4) The order of boiling points is: 1° > 2° > 3° (I > III > II). 1° amine forms more H-bonding with 2 H then 2° amine (1H) and then 3° amine.

2. (1, 2, 3)
(4) is incorrect, since Gabriel method is used to prepare 1° aliphatic amines.
(1) Reductive amination gives better yield.
(2) Although 2° alkyl bromide, elimination of HBr may take place; however it can be prepared by this method.
(3) Azide method is also feasible since $N_3^{\ominus}$ is a good nuclephile.

3. (1, 3, 4)
(2) The order is: $(CH_3)_2NH$ > $(CH_3)NH_2$ > $(CH_3)N$ > NH_3 (2° > 1° >3° > NH_3). Statements (1), (3), and (4) are correct.

4. (3, 4)
On the basis of hybridisation, N (sp^3) of NH_2 with less *s* character should be more basic than N (sp^2) of the imino (=NH) group. However, N of imino group is more basic and it is this nitrogen which is protonated because its conjugate acid is resonance hybrid of three equivalent structure which accounts its unusual stability.

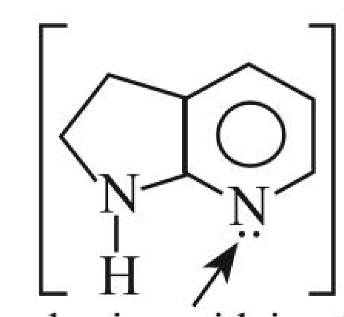


Conjugate acid of guanidine

5. (1, 2, 3)

6. (1, 3, 4)
In (4), Hoffmann's bromamide is given by amides.

7. (2, 4)

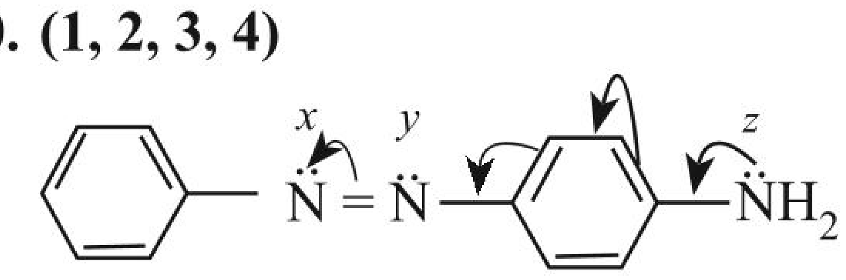
8. (2, 4)
(1) not feasible.
(2) is feasible.
(3) not feasible 

more basic amideine type: electron pair not a part osextet

(4) is feasible by-product in Wurtz reaction.

9. (4) Neutral nature of the compound indicates that it should be a nitro compound. Further zero dipole moment indicates its symmetrical structure, *i.e.*, it should be a benzene derivative having same group ($–NO_2$) in positions *p*-to each other.

10. (1, 2, 3, 4)



x has maximum electron density hence it is most basic. Lone pair of *z* is delocalised. All nitrogen atoms *x, y* and *z* are sp^2 hybridized. The compound has stereoisomerism along N = N

11. (2)

12. (1, 3, 4)
In *p*-$NH_2C_6H_4COOH$, –COOH group is very weak so it can't transfer $H^{\oplus}$ to the weakly basic amino group. All other three form zwitter ions.

13. (1, 2, 4)
Isonitriles (C_6H_5NC) on reduction give 2° amines ($C_6H_5NHCH_3$). All other three methods give aniline.

14. (1, 2, 3)
(1) (I) No delocalisation of LP $\bar{e}$'s on N and sp^3.
(II) Delocalisation of LP $\bar{e}$'s of one N atom, but no delocalisation of LP $\bar{e}$'s on second N.
(III) No delocalisation of LP $\bar{e}$'s of N, but sp^2.
(2) (I) No delocalisation of LP $\bar{e}$'s of N.
(II) Delocalisation of LP $\bar{e}$'s of N by (C = O) group.

(3) (I) No delocalisation of LP $\bar{e}$'s of N.

(II) Delocalisation of LP $\bar{e}$'s with benzene ring.

(4) The order is (I) > (III) > (II).

(I) No delocalisation and sp^3.

(II) Delocalisation of LP $\bar{e}$'s of N and sp^2.

(III) Delocalisation of LP $\bar{e}$'s of one N but no delocalisation of second N atom LP $\bar{e}$'s and sp^2.

15. (1, 2, 3, 4)

(1) Hoffmann's bromamide.

(2) Carbylamine

(3) Carbocation, ring expansion.

16. (1, 2, 4)

In *p*-aminophenol all the four positions (2, 3, 5 and 6) can be coupled (positions 2 and 6 in presence of $H^{\oplus}$ and positions 3 and 5 in presence of $OH^{\ominus}$).

17. (2, 4)

It is a benzidine rearrangement reaction.

Refer to section 7.3)

18. (2, 3, 4)

(1) gives C_2H_5CN, others give isocyanide

19. (2, 3, 4)

factual

20. (2, 3, 4)

21. (2, 4)

2º amine and phenol give this test.

22. (1, 2, 4)

23. (1, 2, 3, 4)

factual

24. (2, 3)

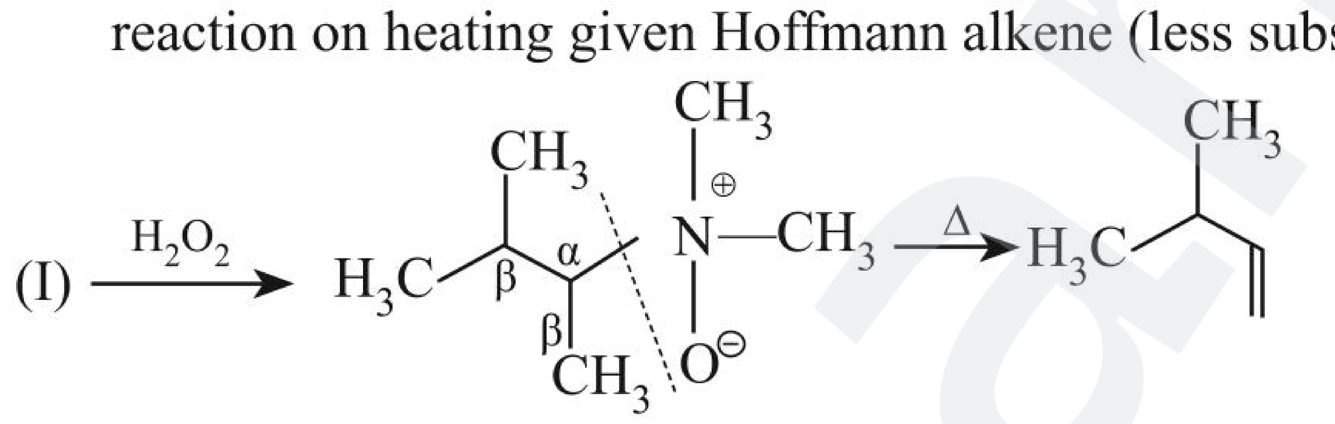
factual.

25. (1, 3, 4)

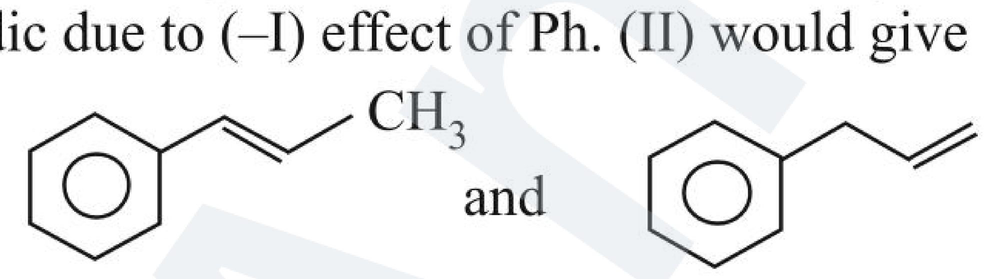
factual.

26. (1, 3)

(1) The oxidation of 3º amine to amine oxide followed by Cope reaction on heating given Hoffmann alkene (less substituted.)



(2) (II) will not give Hoffmann alkene. Benzylic H atom is more acidic due to (–I) effect of Ph. (II) would give

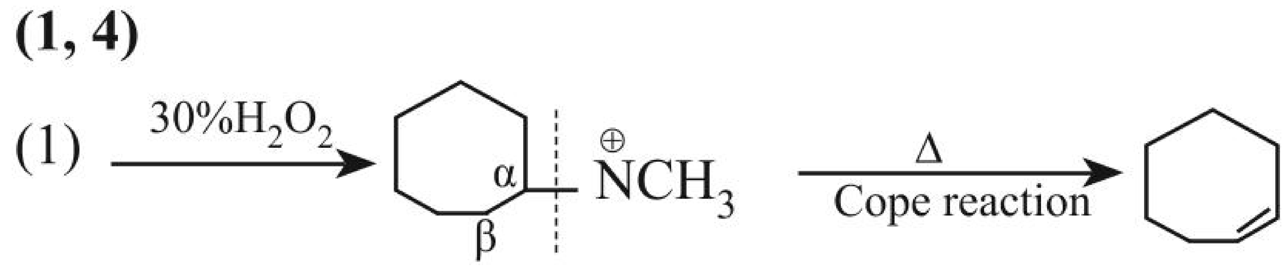


(Stability of benzyl $C^{\oplus}$) Hoffmann alkene.

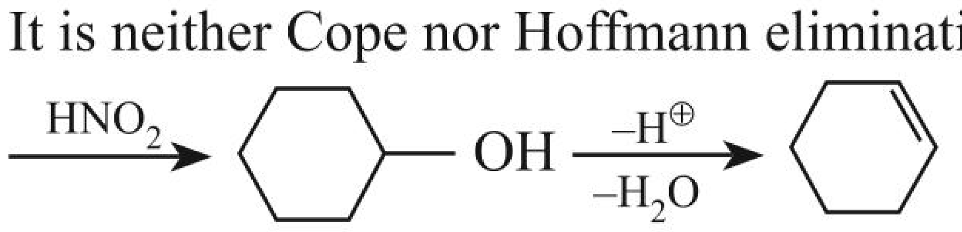
(3) (III) will give Hoffmann alkene $CH_2=CH_2$.

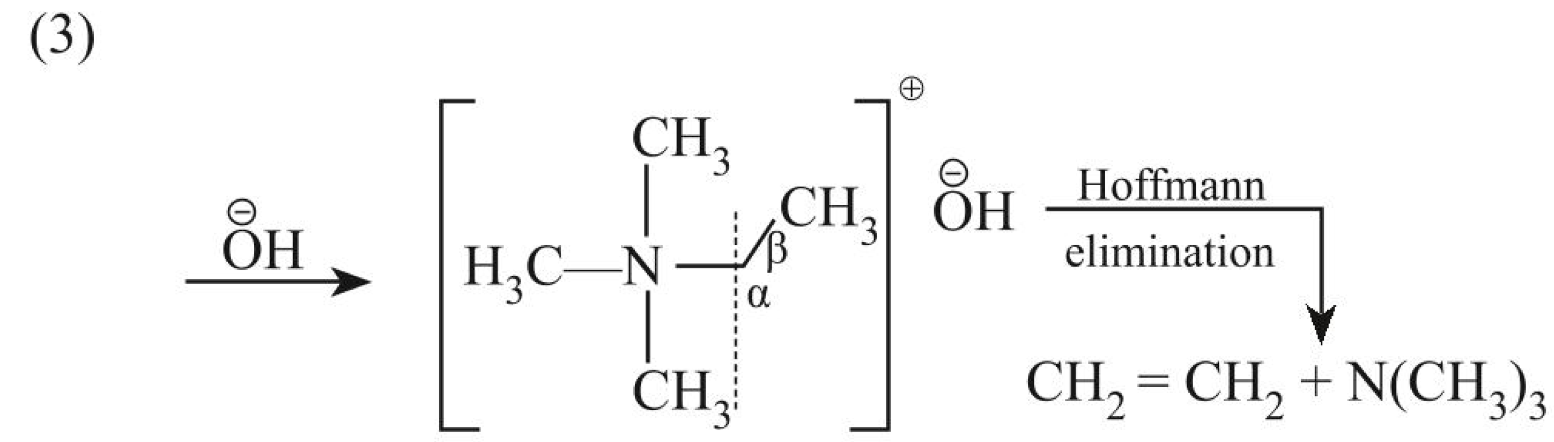
(4) (IV) will not give Hoffmann alkene (Cope reaction). Same explanation as in (2) above.

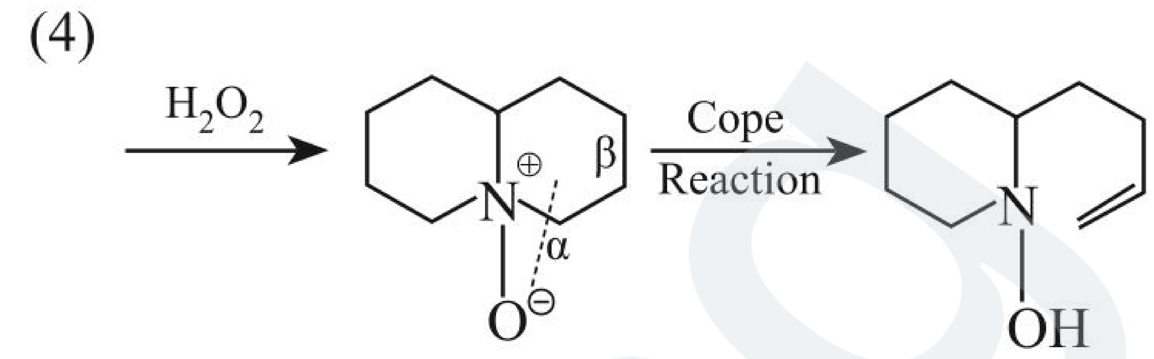
27. (1, 4)



(2) It is neither Cope nor Hoffmann elimination reaction







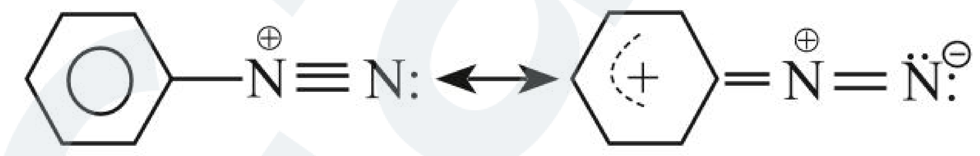
28. (2, 4)

(2) Due to steric inhibition of resonance, lone pair of electrons on N-atom are not delocalised. Hence I is more basic than II

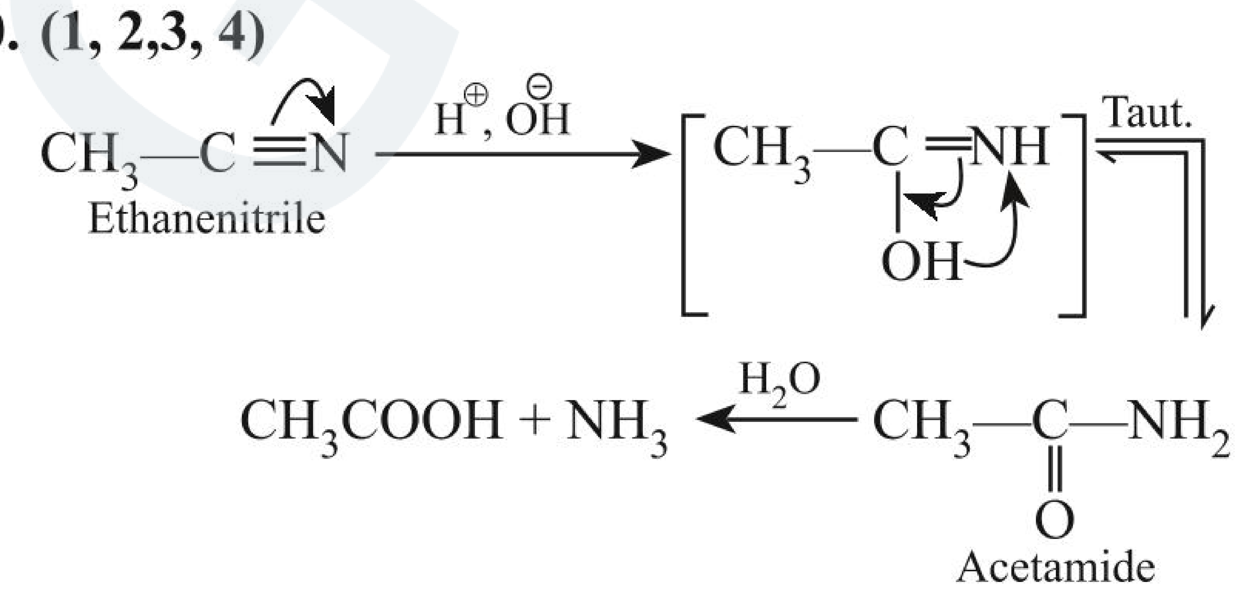
(4) same explanation as in (2)

29. (1, 2, 3)

(1), (2), (3) are correct and (2), (3) are the explanations of (1).



30. (1, 2,3, 4)

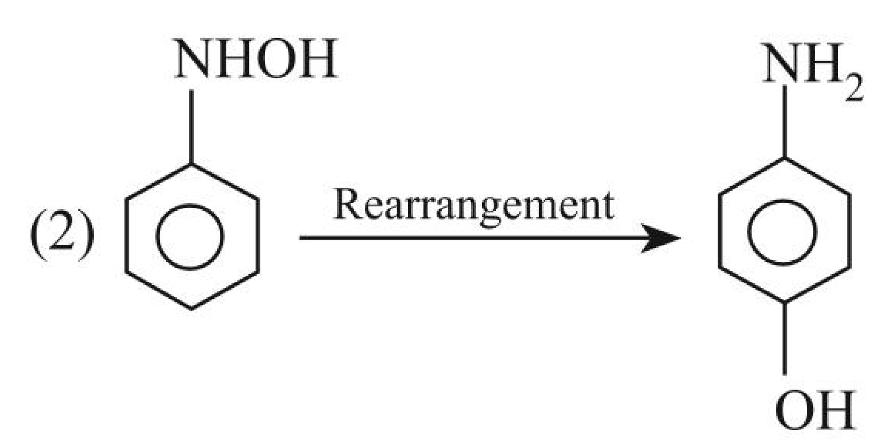


31. (1, 2, 3)

Diazonium ion can be replaced by H by (3) H_3PO_2 or (3) Na_2SnO_2 or (3) C_2H_5OH and heat.

32. (1, 2)

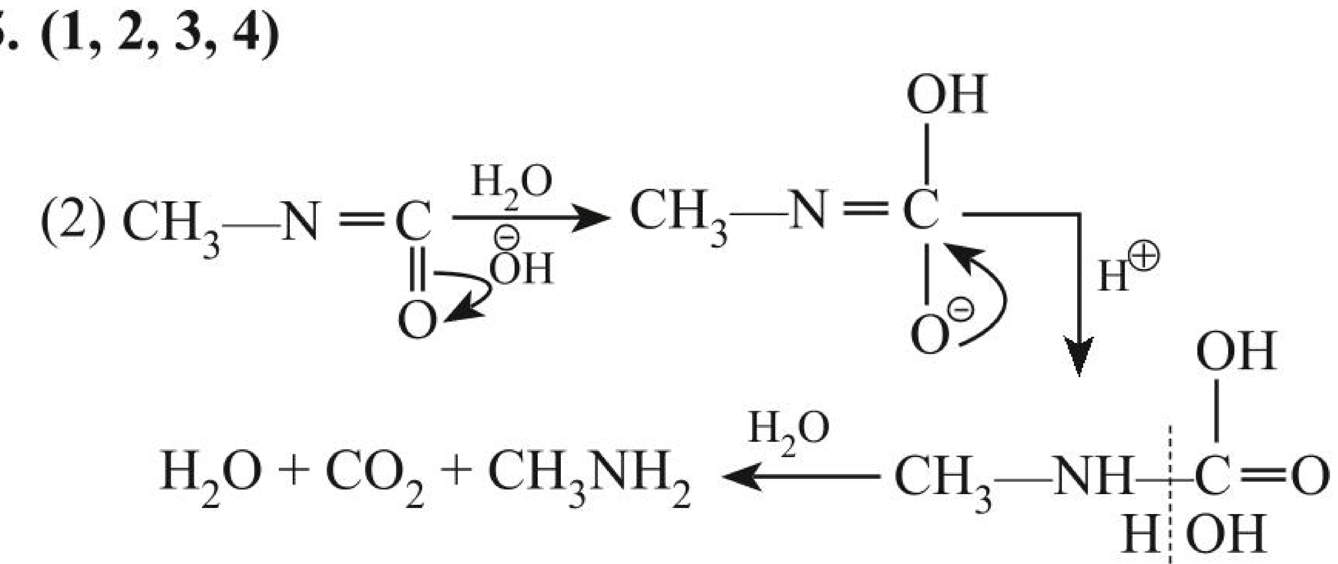
(1) $PhNH_2$



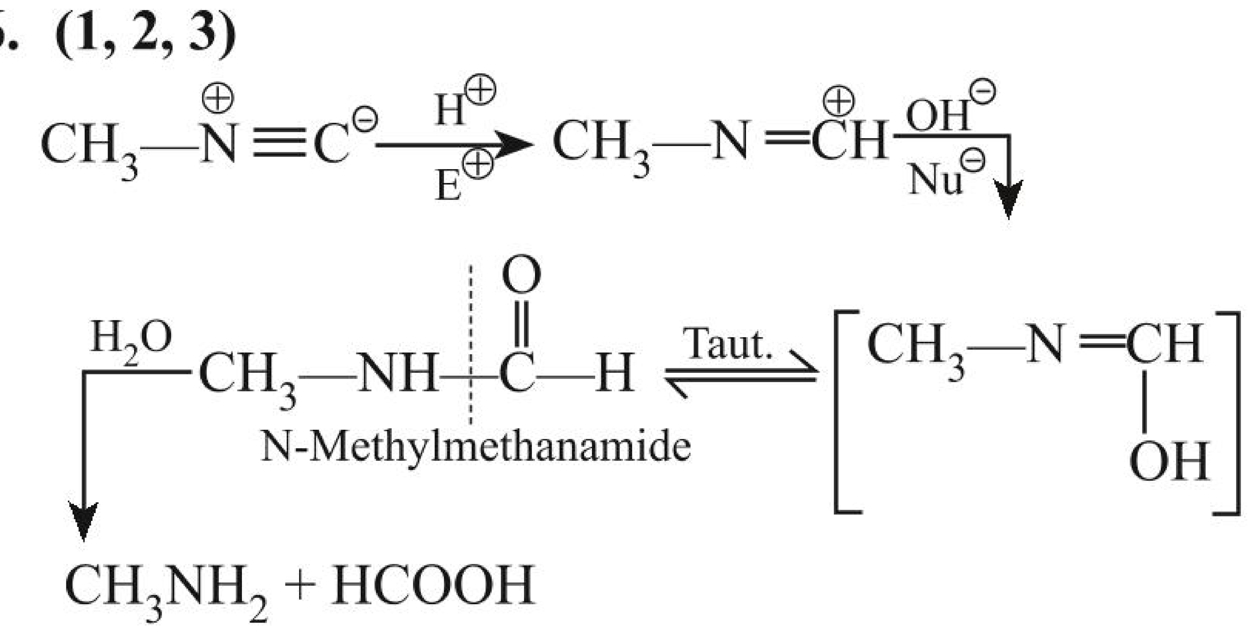
33. (1, 3, 4)

34. (1, 2, 3, 4)

35. (1, 2, 3, 4)



36. (1, 2, 3)



37. (2, 3)

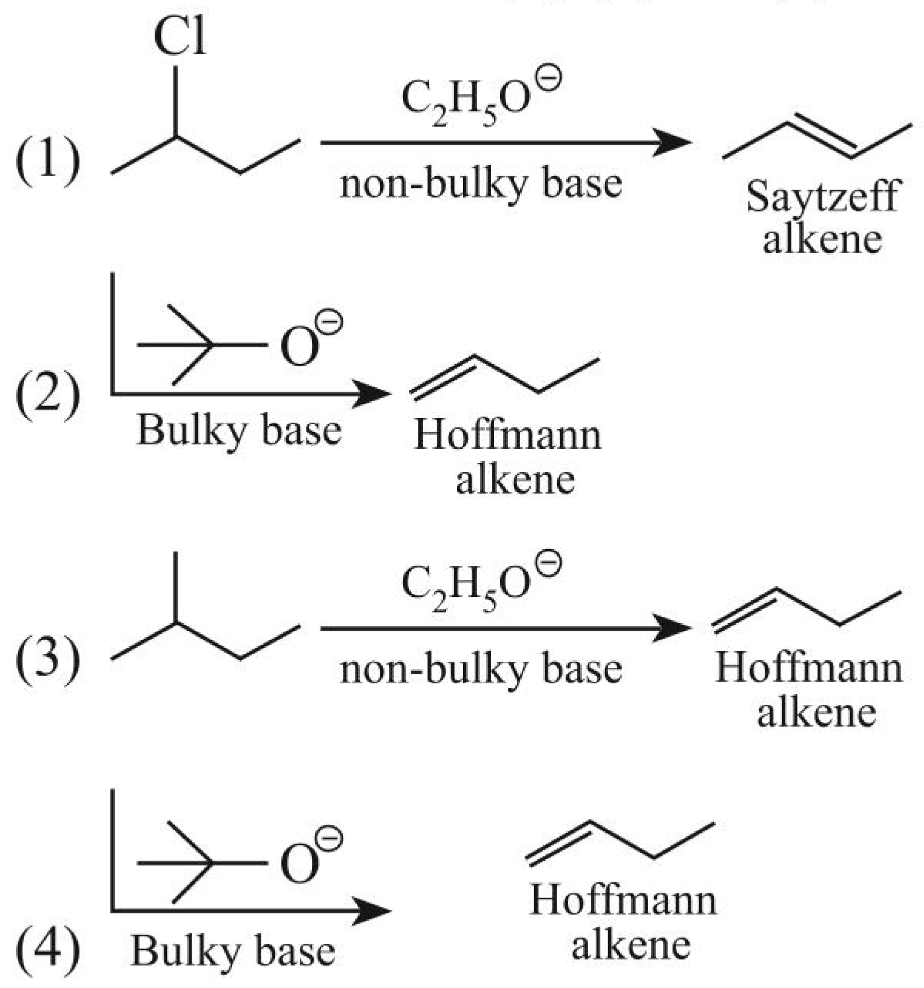
(1) PhNHOH (Phenyl hydroxylamine)

(2) PhN=NPh (Azobenzene)

38. (2, 3, 4)

RF gives Hoffmann alkene (less substituted) whether base is bulky or non-bulky. whereas RX (X= Cl, Br, I) gives Saytzeff alkene (more substituted) if base is non-bulky and gives Hoffmann alkene if base is bulky.

Hence the answer is (2), (3) and (4).

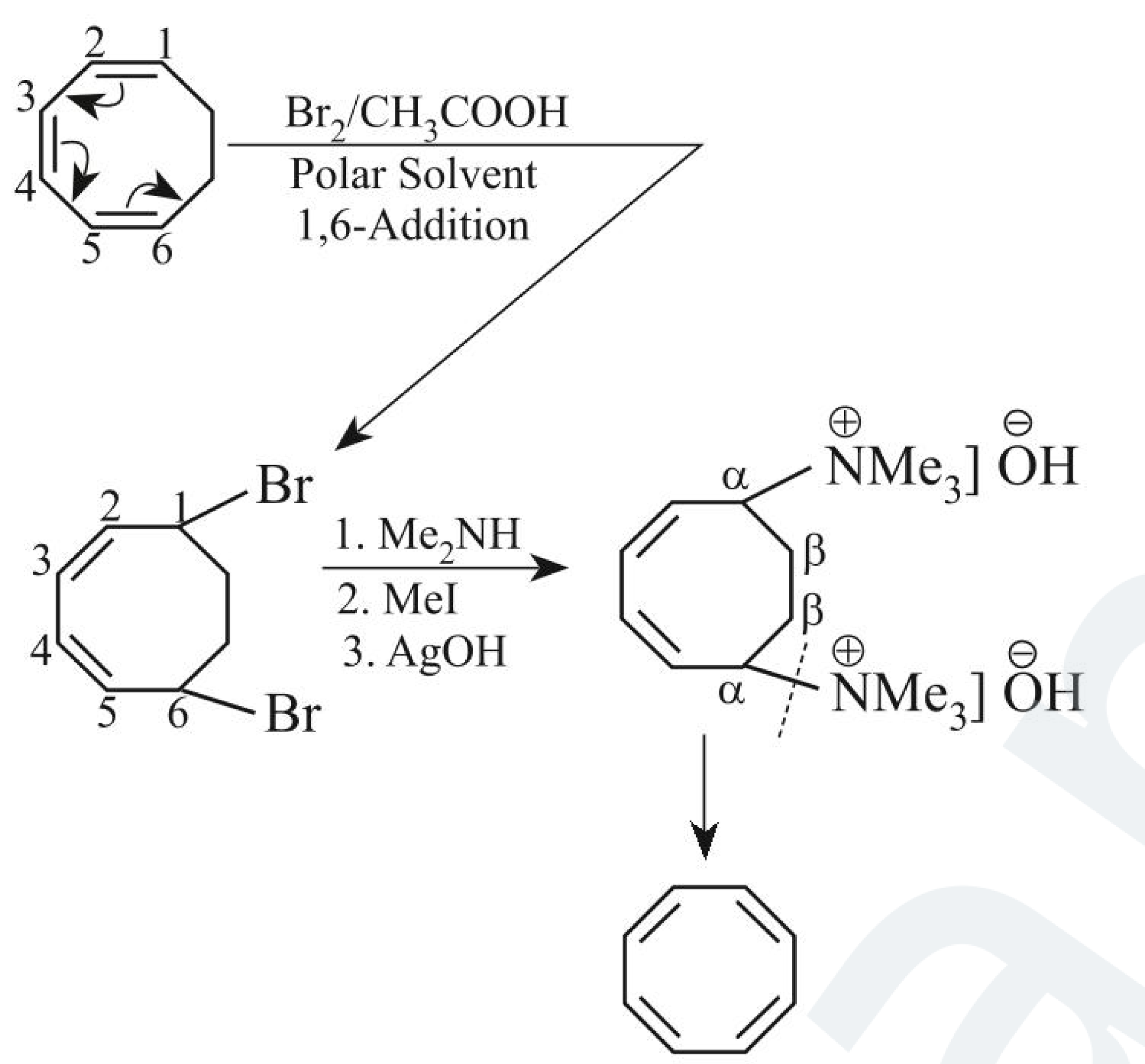


39. (1, 2, 3)

40. (1, 2, 3, 4)

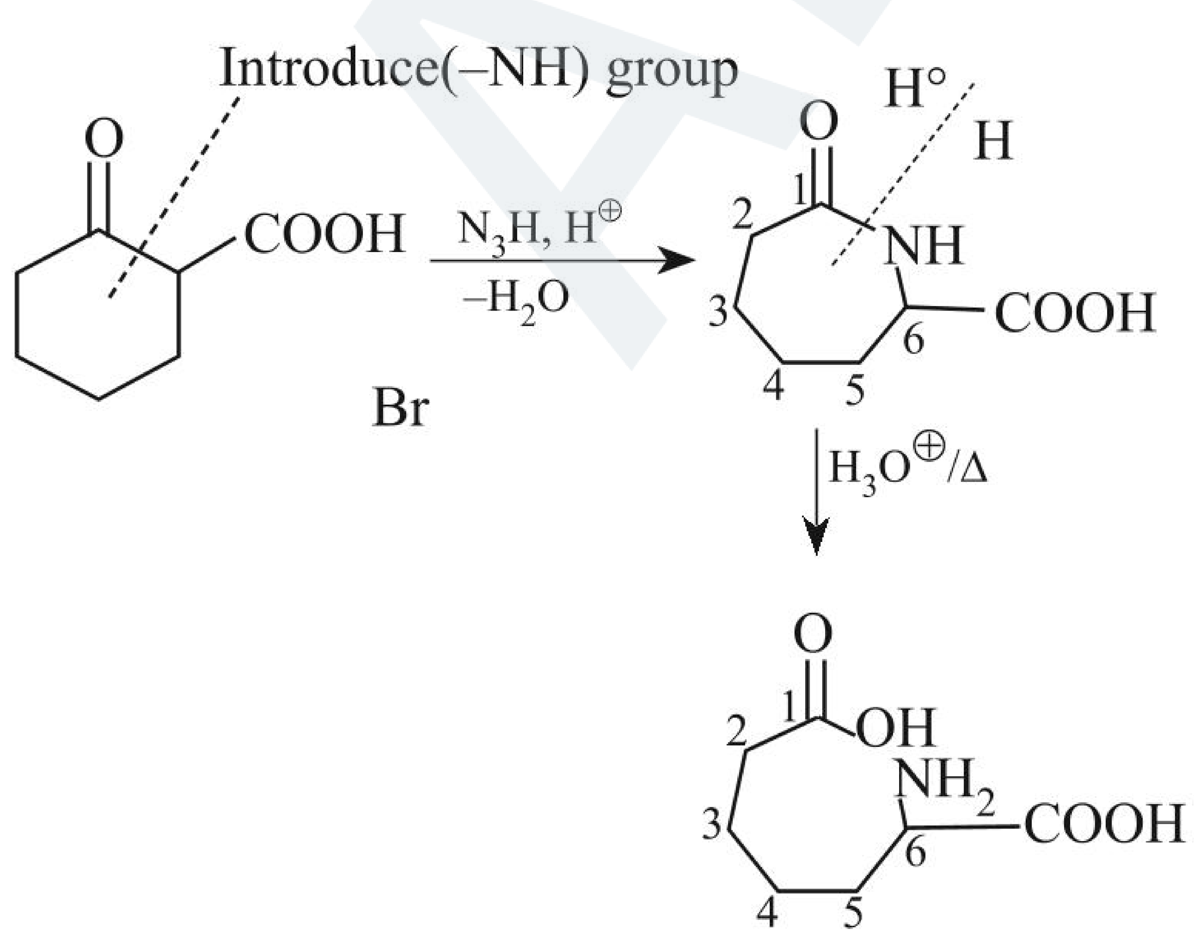
41. (1, 4)

Reaction (I) is an example of Hoffmann exhaustive methylation and elimination:



Reaction II is an example of. Claisen Schmidt rearrangement type reaction of aldehydes and ketone with $N_3H/H^\oplus$. Keto group is more reactive than (–COOH) group, so reaction of $N_3H/H^\oplus$ will occur preferentially at (C═O) group.

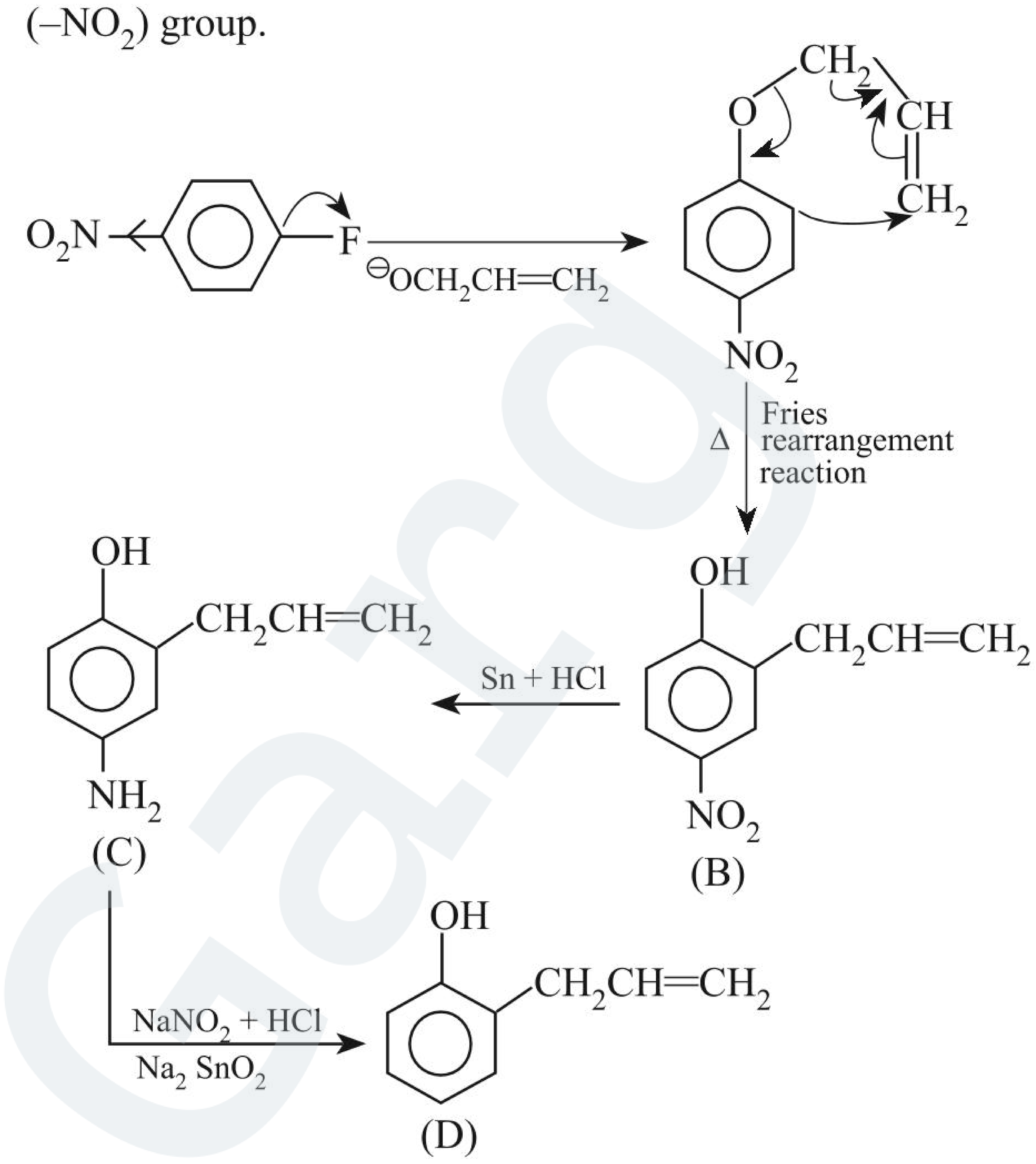
Introduce –NH group between (C═O) and (COOH) group.



(Y)

42. (1, 4)

(2) ArSN reaction is favoured by strong EWG at *o*- and/or *p*-position ($-NO_2$) group.

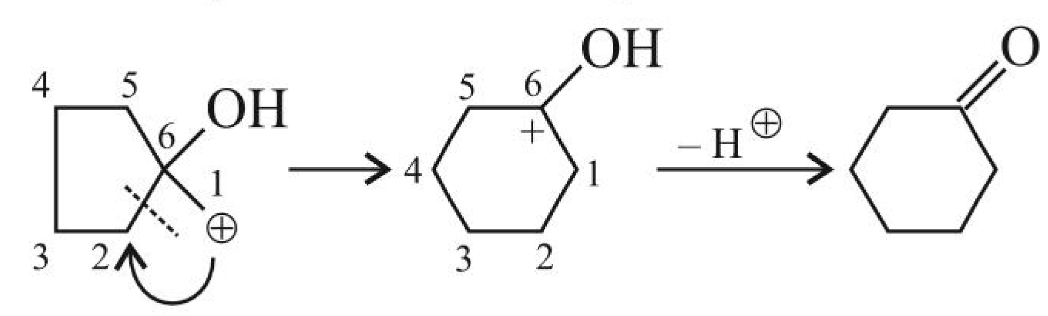


43. (1, 2, 4)

44. (1, 2)

45. (3, 4)

(3) The ring extension takes place.



(4) It becomes optically inactive due to the formation of racemic mixture.

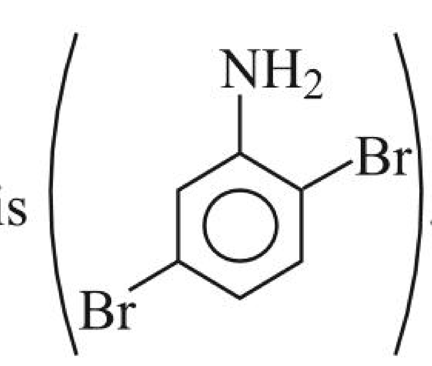
46. (1, 2, 3, 4)

Linked Comprehension Type

Paragraph 1

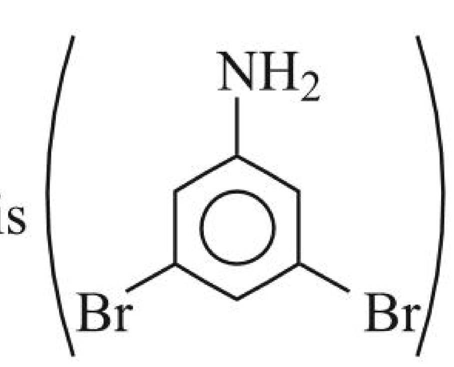
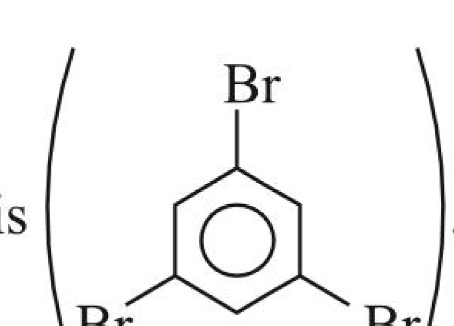
1. (1) **2. (2)** **3. (2)** **4. (3)**

In compound (A), the (—NH_2) group is removed and from the percentage of Br in (A), it is suggested that two (Br) groups are present in (A). The formation of one mono-nitro derivative from (B) suggests that two (Br) groups are present at *para*-position (OMP = 231).

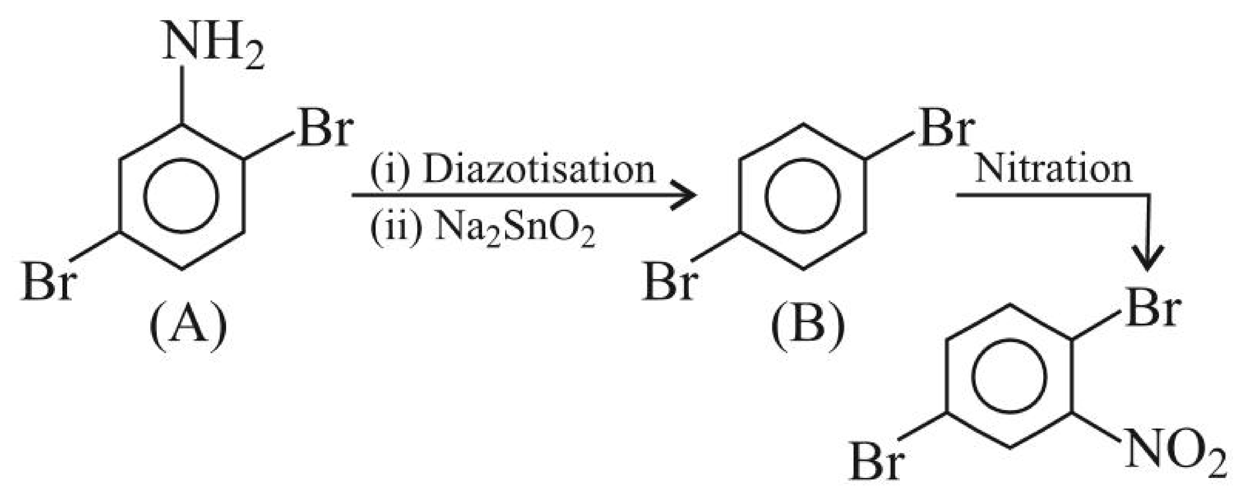
So compound (A) is .

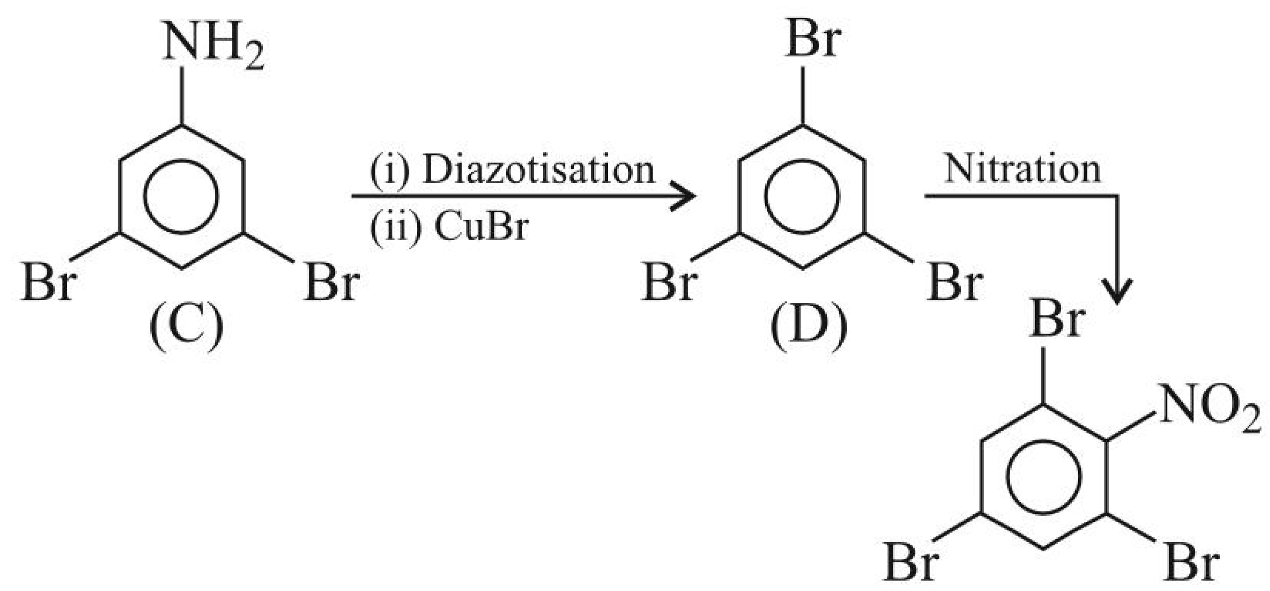
In compound (C), the (—NH_2) group is removed and one more (Br) group is introduced in (C); this suggests that compound (D) contains three (Br) groups, which is confirmed from the percentage of Br in (D).

The formation of one mono-nitro derivative from (D) suggests that three Br groups are present at symmetrical position in (D) (AUS = 231).

So compound (C) is  and (D) is .

Reactions:

i. 

ii. 

Calculation of number of Br in (A), (B), and (D).

In (A): 100 gm of compound contains = 63.7 gm of Br

251 gm of compound contains = $\dfrac{63.7 \times 251}{100}$ gm

of Br = $\dfrac{63.7 \times 251}{100 \times 80}$ mol of Br = 1.99 ≈ 2 mol Br.

In (B): Molar mass of (B) ($C_6H_4Br_2$) = 236 gm

Moles of Br in (B) = $\dfrac{67.80 \times 236}{100 \times 80} \approx 2$ mol Br

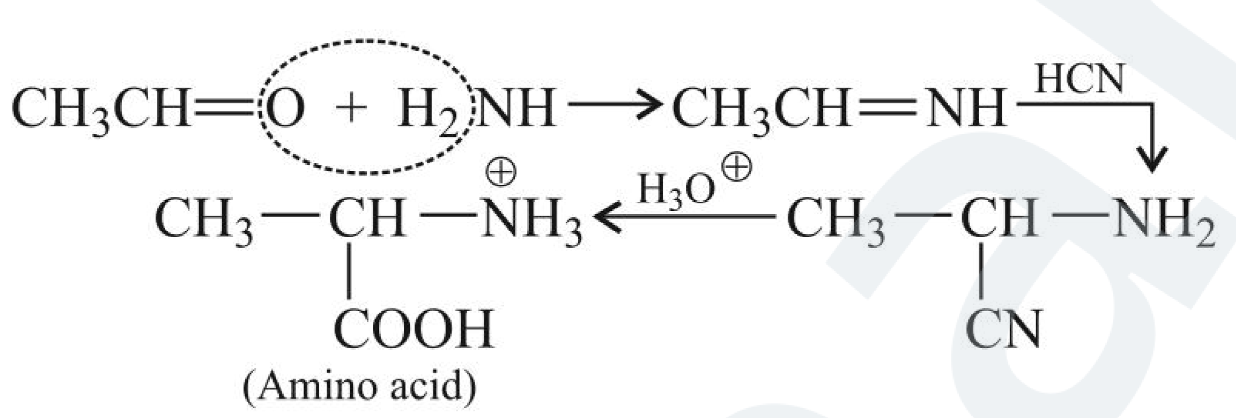
In (D): Molar mass of (D) ($C_6H_3Br_3$) = 315 gm

Moles of Br in (D) = $\dfrac{76.4 \times 315}{100 \times 80}$ = 3 mol Br

Paragraph 2

5. (2) **6. (1)** **7. (3)**

Compound (X) is $CH_3-\overset{\overset{O}{\|}}{C}-H$.



When partial neutralisation of alanine occurs,

Then, $pH = pK_a + \log\left[\dfrac{\text{salt}}{\text{acid}}\right]$

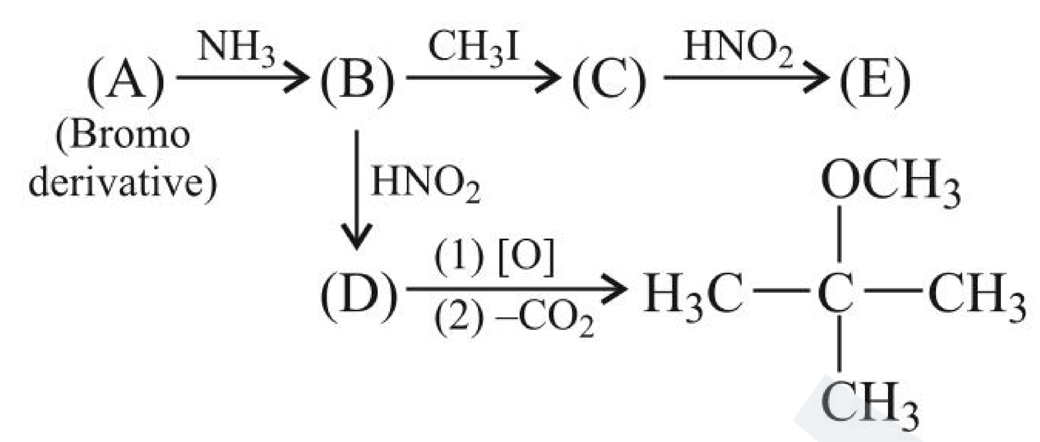
[salt] = [acid]

$pH_1 = pK_{a1}$ and $pH_2 = pK_{a2}$

$\therefore\ pH = \dfrac{pK_{a_1} + pK_{a_2}}{2} = \dfrac{9.7 + 2.3}{2} = \dfrac{12.0}{2} = 6.0$

Paragraph 3

8. (1) **9. (1)** **10. (2)** **11. (2)** **12. (1)**



i. 2-Methoxy-2-methyl propane is obtained by the oxidation of (D) followed by decarboxylation, and thus (D) is

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OCH_3}{|}}{C}}-CH_2CH_2OH\cdot$$

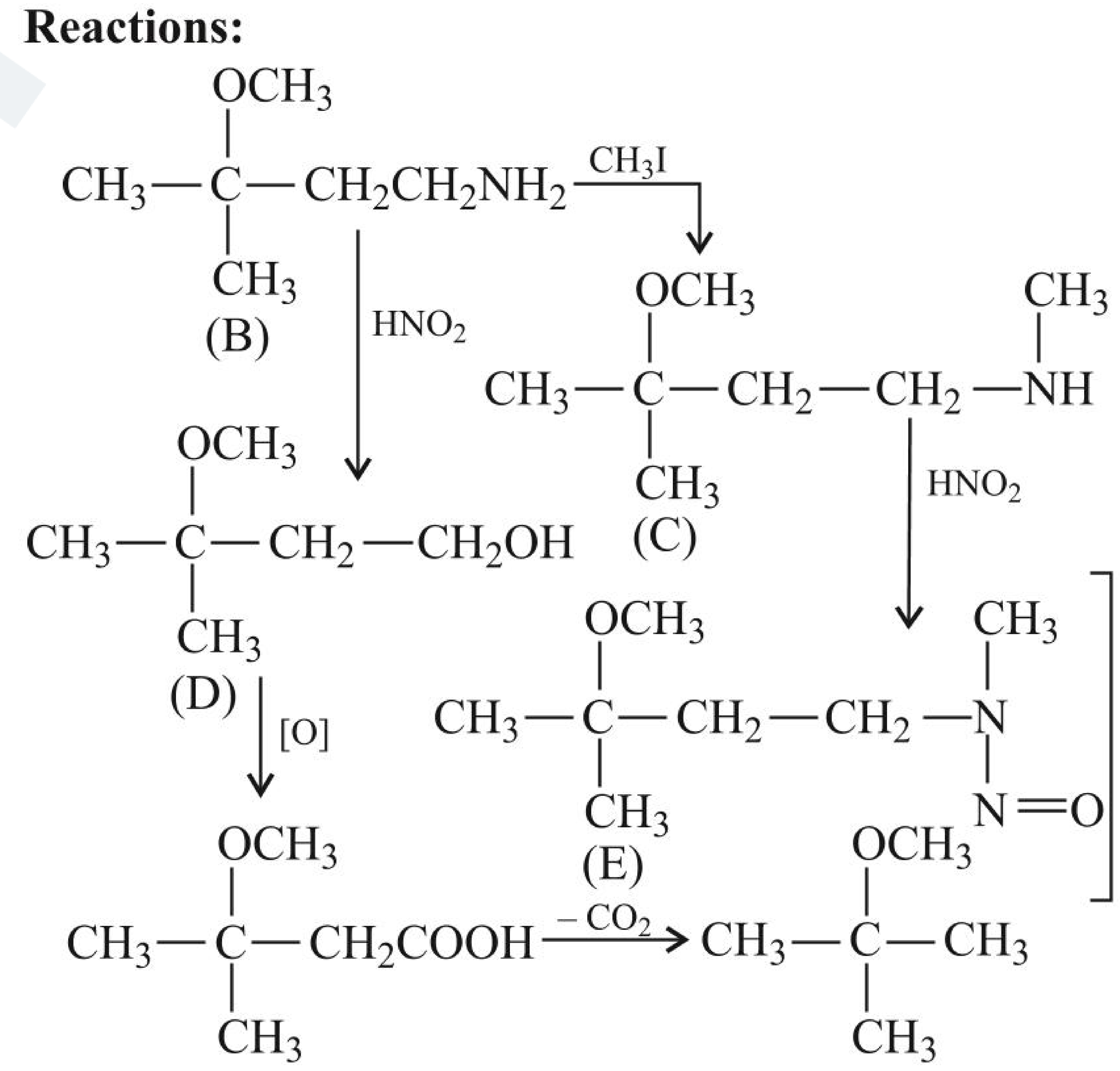
ii. (D) is formed by the action of HNO_2 on (B), thus (B) is

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OCH_3}{|}}{C}}-CH_2CH_2NH_2\cdot$$

iii. (B) is formed by the action of NH_3 over (A), a bromoderivative.

$$(A) \Rightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OCH_3}{|}}{C}}-CH_2CH_2Br\cdot$$

Reactions:



Paragraph 4

13. (2) **14. (2)** **15. (1)** **16. (1)** **17. (3)**
18. (2)

Percentage of N = ?

Total acid $= 50 \times \dfrac{1}{10} = 5$ mEq.

Excess acid $= 30 \times \dfrac{1}{10} = 3$ mEq.

Acid used = 5 – 3 = 2 mEq.

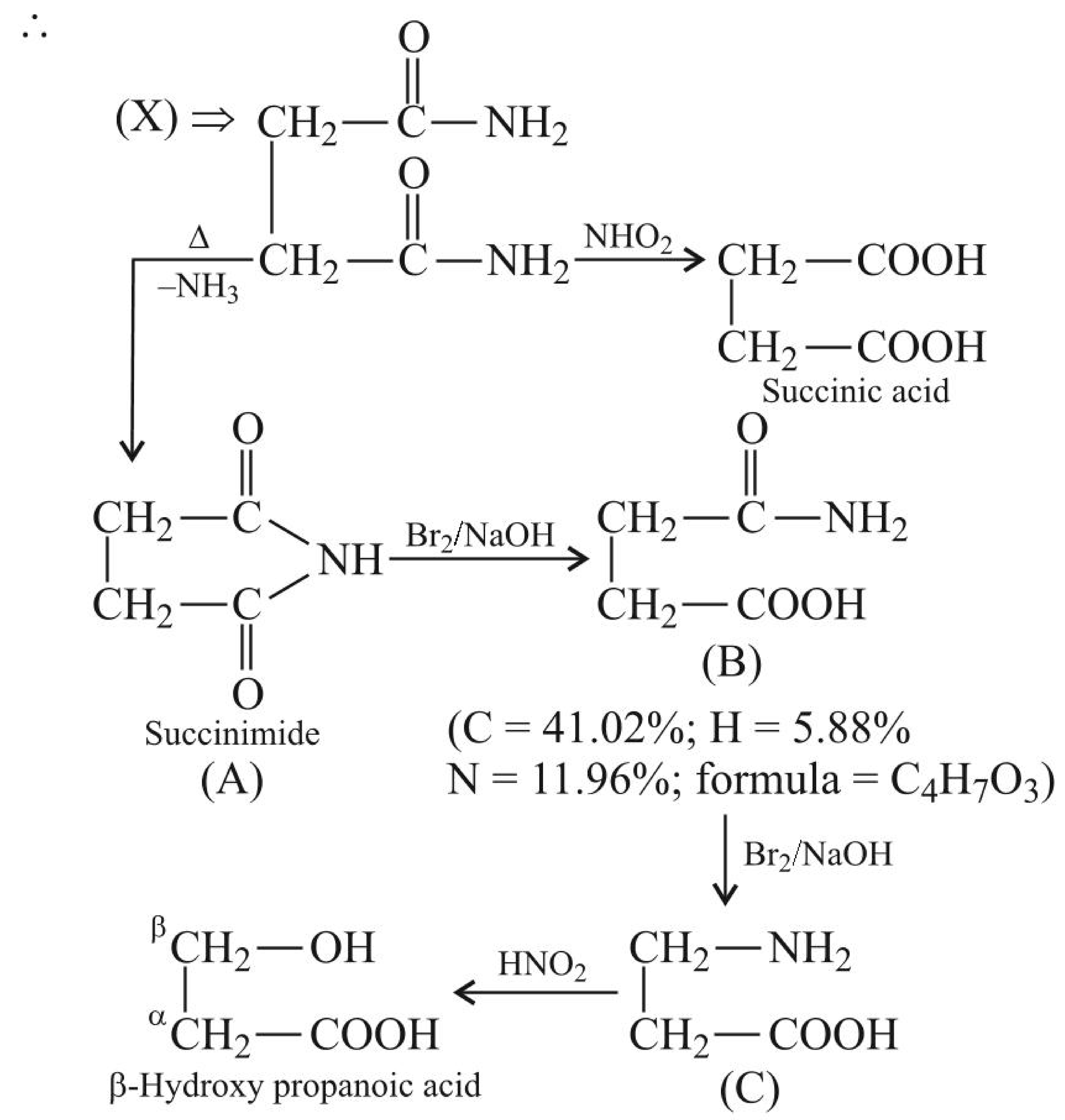
Percentage of N $= \dfrac{1.4 \times \text{mEq. of acid used}}{\text{Weight of compound}} = \dfrac{1.4 \times 2}{0.116} = 24.38\%$

C = 41.37% H = 6.89% N = 24.38%

O = 100 – (41.37 + 6.89 + 24.38) = 27.36

Formula = $C_4H_8O_2N_2$; degree of unsaturation = 2°.

∴



Matrix Match Type

1. **(a → q, r; b → p; c → s; d → t)**

(a → q, r) α-Amino acid on heating gives piperazine and the product exhibits three stereo-isomers (*cis* and *trans*) and *cis* is optically active.

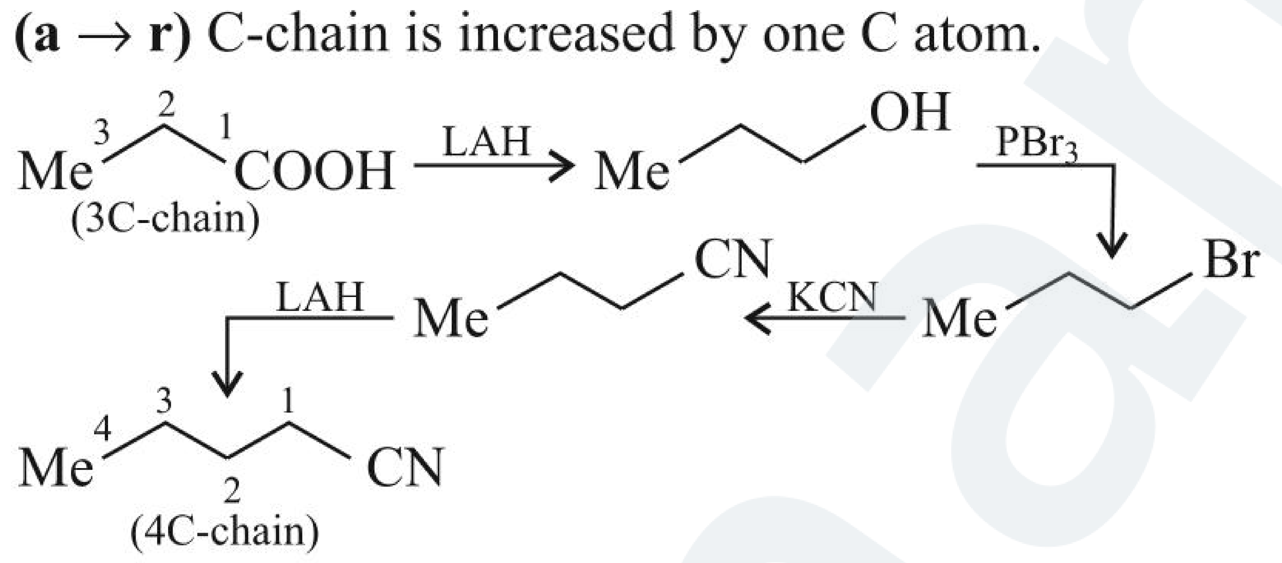
(b → p) It is also α-amino acid. It also gives piperazine on heating but this type does not give any stereoisomers since it does not have any alkyl group.

(c → s) It is γ-amino acid. So on heating it gives five-membered lactam.

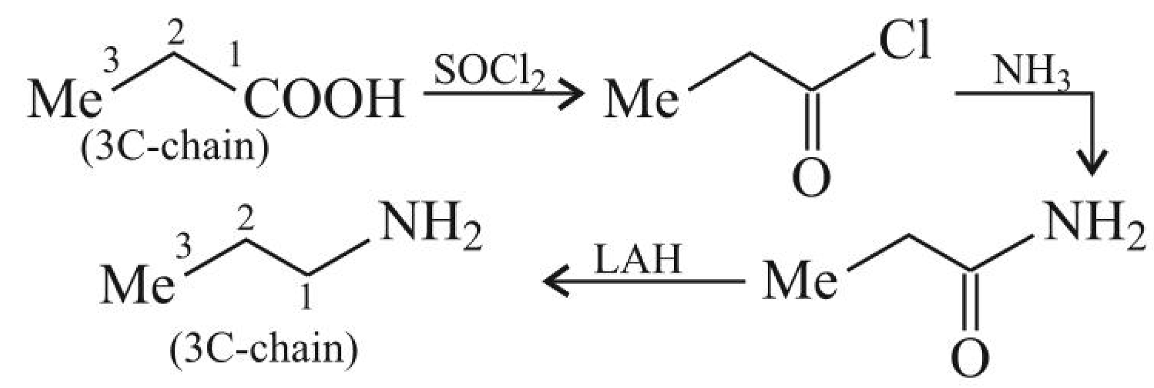
(d → t) It is δ-amino acid. So on heating it gives six-membered lactam.

2. **(a → r; b → s; c → p; d → q; e → u ; f → t)**

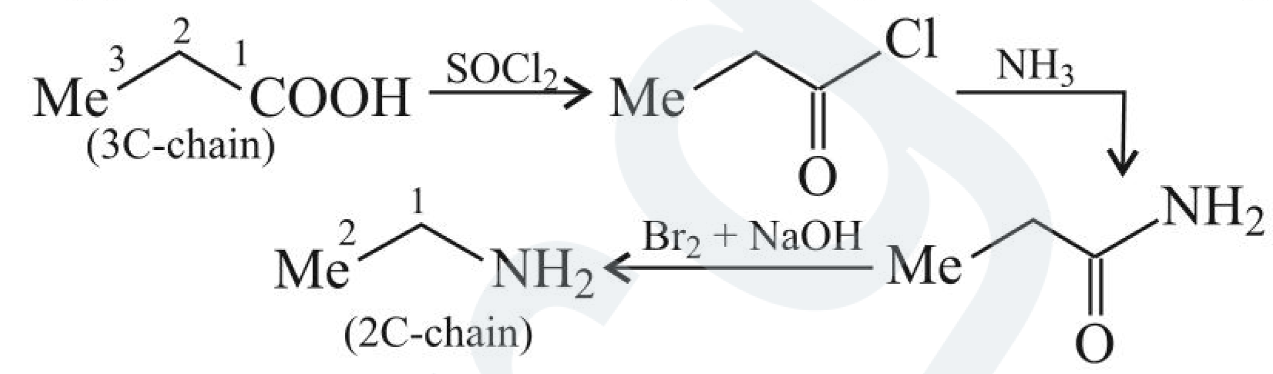
(a → r) C-chain is increased by one C atom.



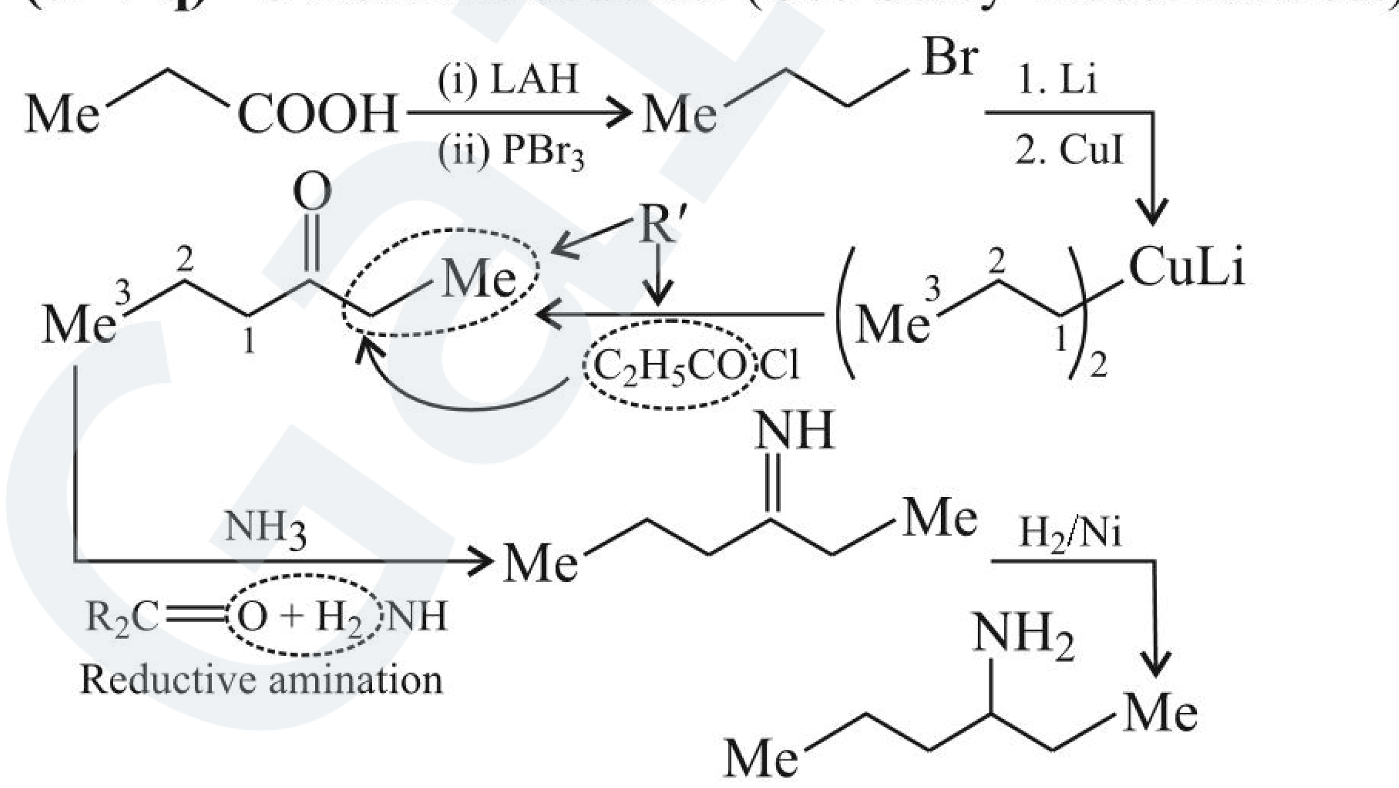
(b → s) C-chain is unchanged.



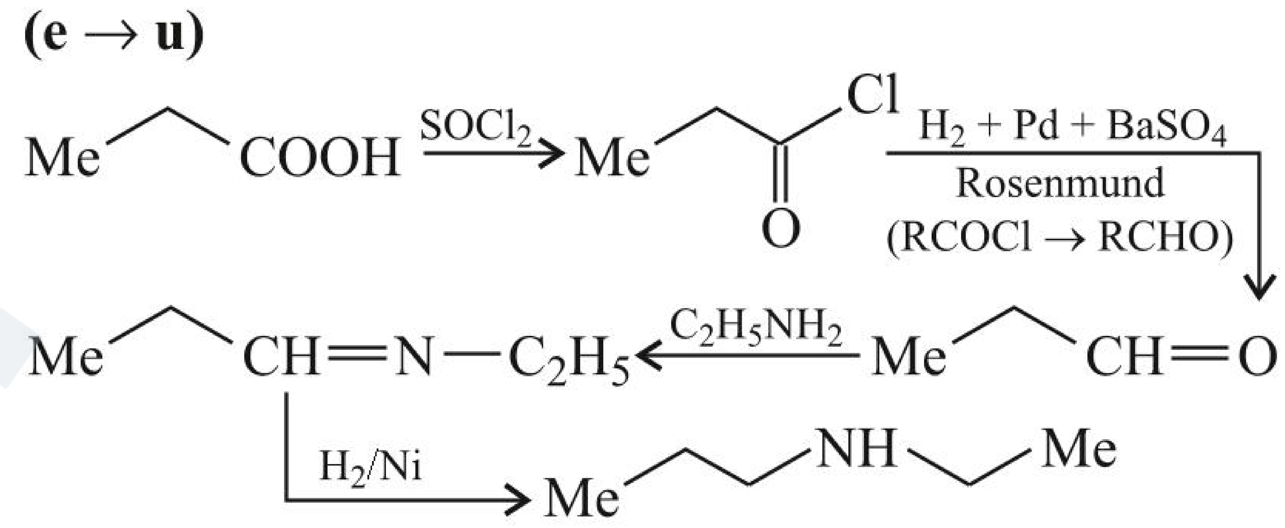
(c → p) C-chain is decreased by one C (use Hofmann degradation).



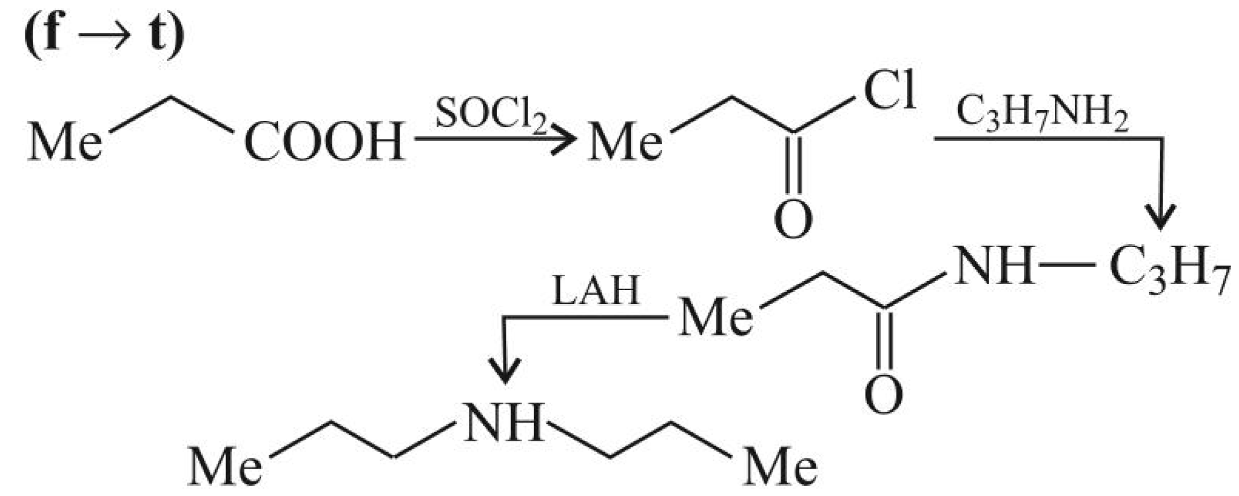
(d → q) C atom has doubled. (Use Corey–House method.)



(e → u)



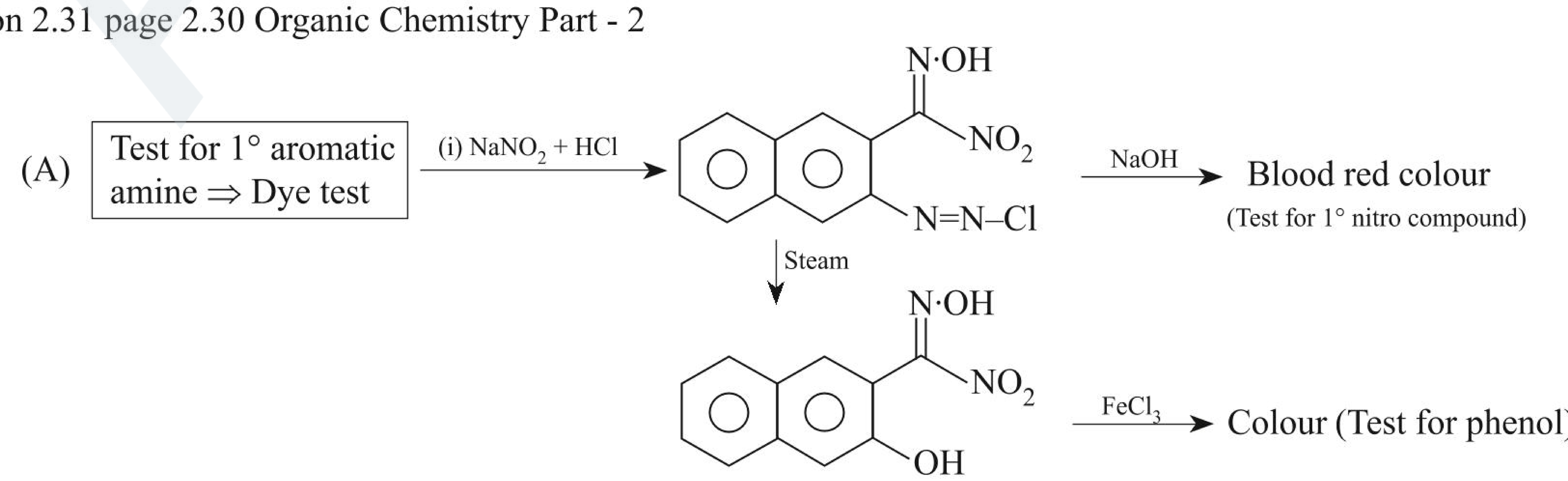
(f → t)



3. **(a → ii, p, r; b → i, q, s; c → ii, iii, t; d → iv, t)**

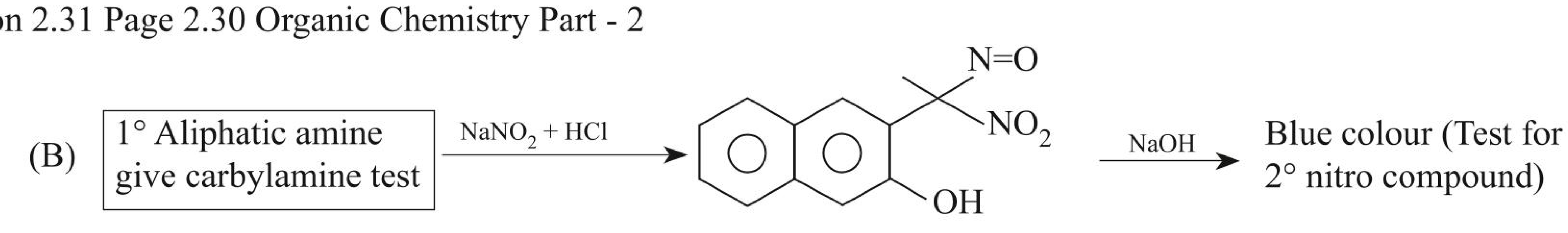
(a → ii, p, r)

Refer to section 2.31 page 2.30 Organic Chemistry Part - 2



(b → i, q, s)

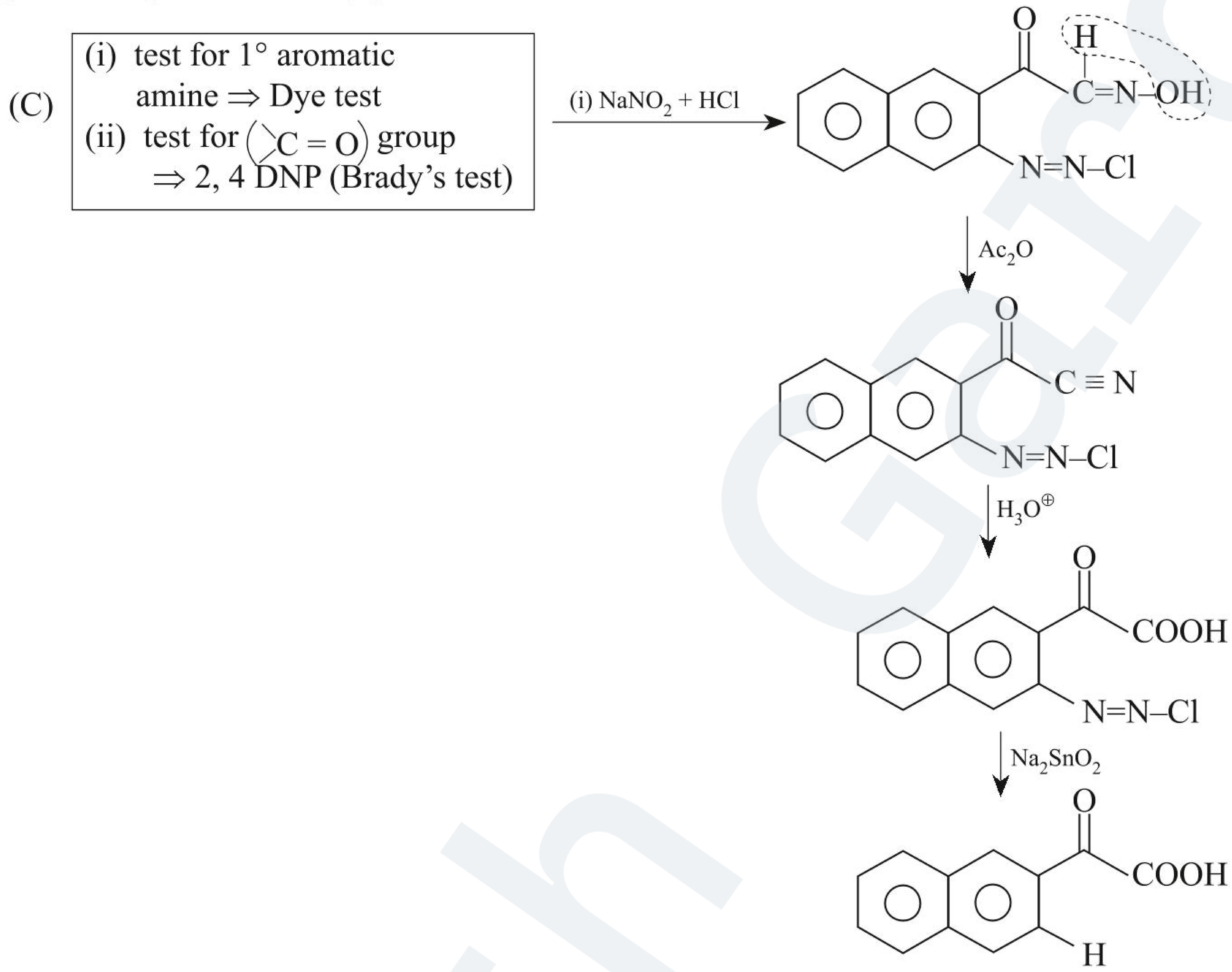
Refer to section 2.31 Page 2.30 Organic Chemistry Part - 2



(Test for alcohol, ⇒ CAN test)

(c → ii, iii, t)

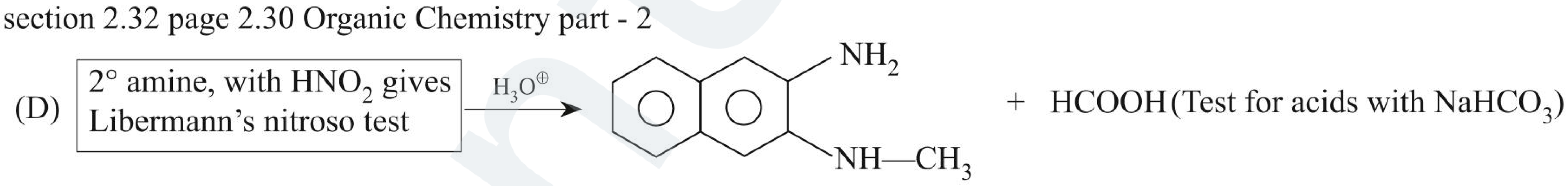
Refer to section 5.28 page 5.20 Organic Chemistry part - 2



(Test for acids with NaHCO$_3$)

(d → iv, t)

Refer to section 2.32 page 2.30 Organic Chemistry part - 2



Numerical Value Type

Refer for all Section 7.17

1. (3) Piperazine is formed
(a) (+) cis (b) (–) cis (c) Meso form of trans

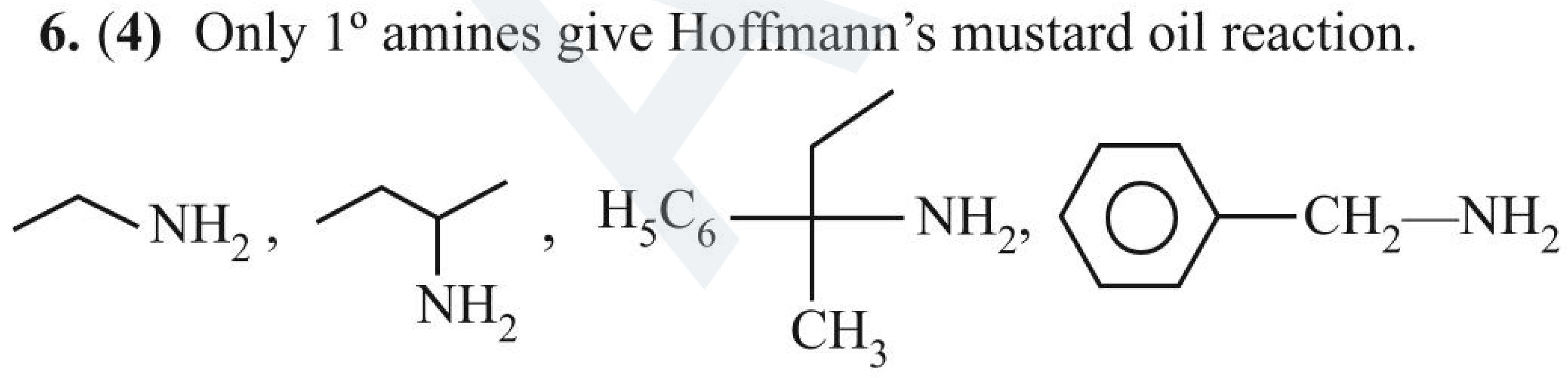
2. (2) cis & trans (α, β-unsaturated acid)

3. (4) I, II, III, IV (cyclic amide)

4. (2) I, II (five membered cyclic amide)

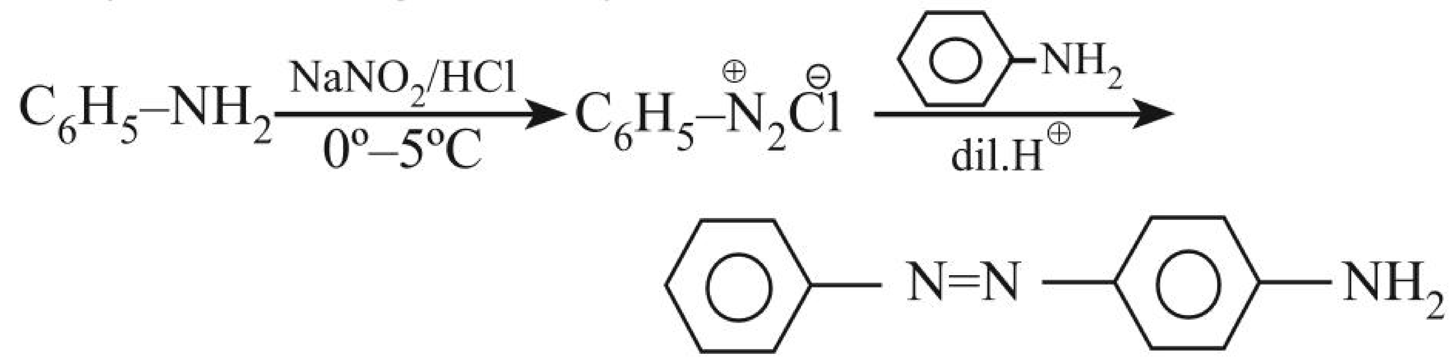
5. (2) III, IV (six membered cyclic amide)

6. (4) Only 1° amines give Hoffmann's mustard oil reaction.



7. (3) Only 1° amines give carbyl amine reaction.

8. (5)



9. (5) Five compounds (2, 3, 5, 6, and 7) are more basic than aniline.

(2) ⇒ No delocalisation of lone pair of electrons on N-atom

(3) ⇒ (–OCH$_3$) is EDG (+ R > – I).

(5) ⇒ Two N-atom with lone pairs

(6) ⇒ Three N-atoms with lone pairs

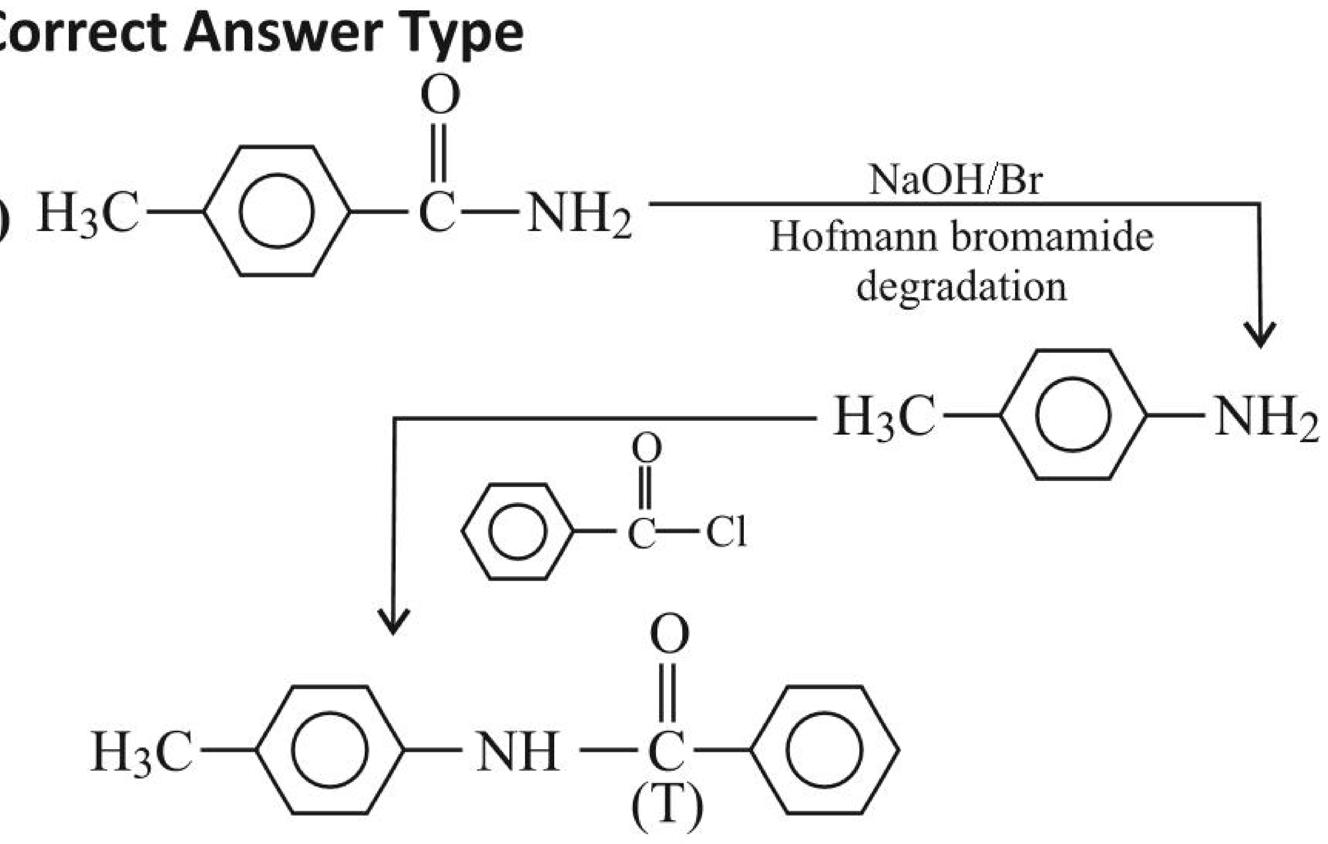
(7) ⇒ No delocalisation of lone pair of electrons on N-atom. Moreover 1° aliphatic amines are more basic than aniline

Archives

JEE Advanced

Single Correct Answer Type

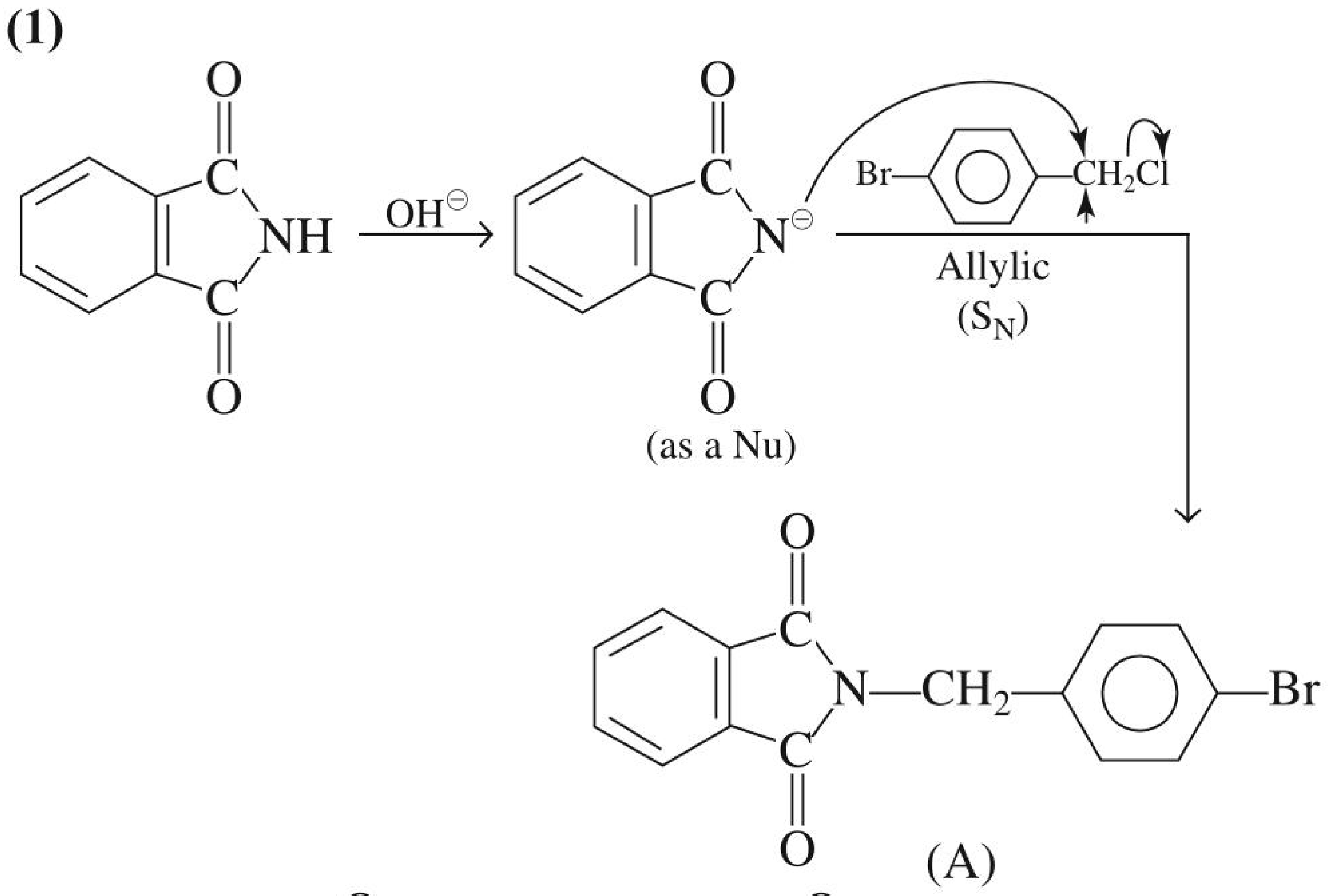
1. (3)

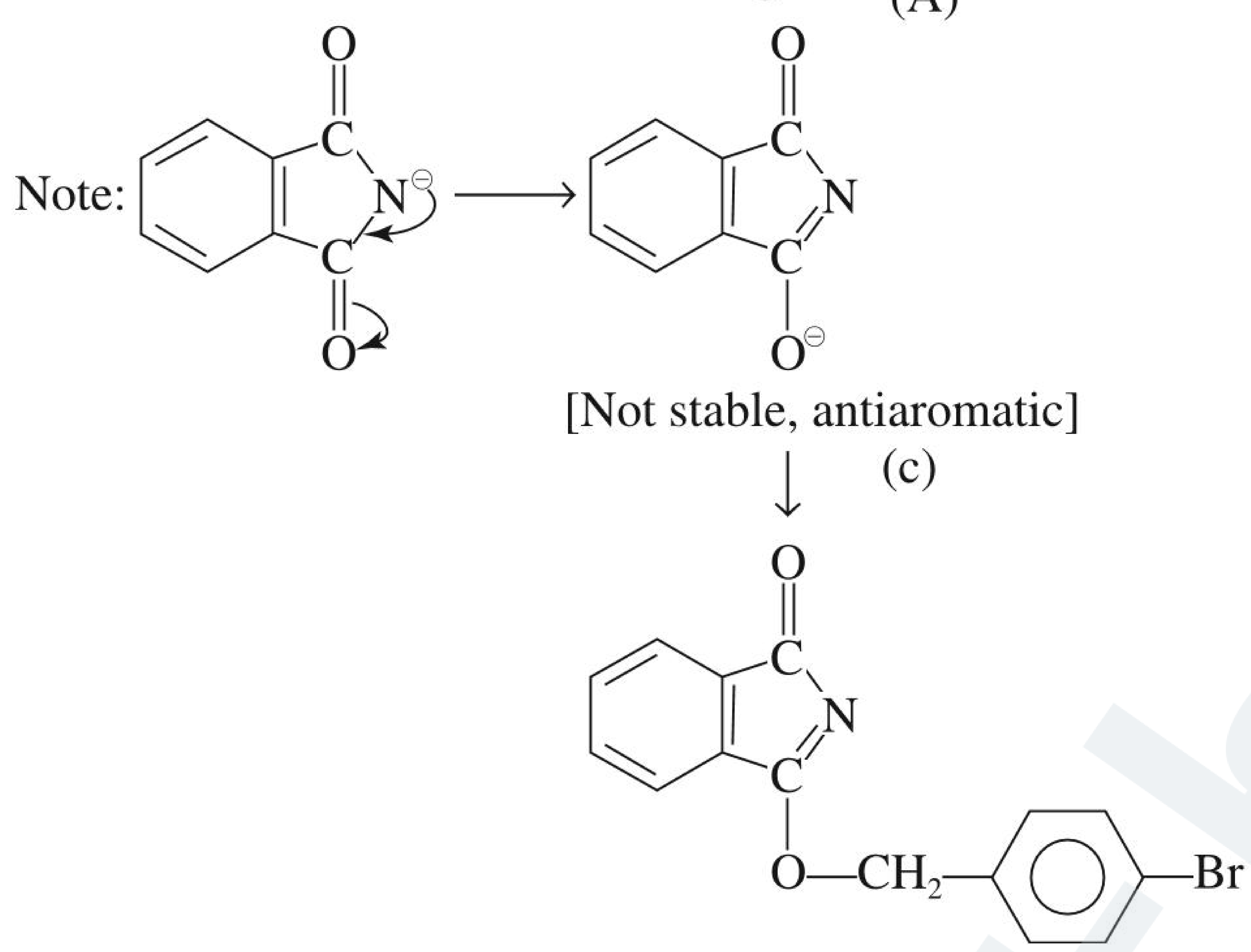


2. (3) 1° aromatic amine gives diazonium salt which couples with β-naphthol in basic medium to give brilliant colour dye.

So compound is (3) (H_3C–⟨◯⟩–NH_2)

3. (1)





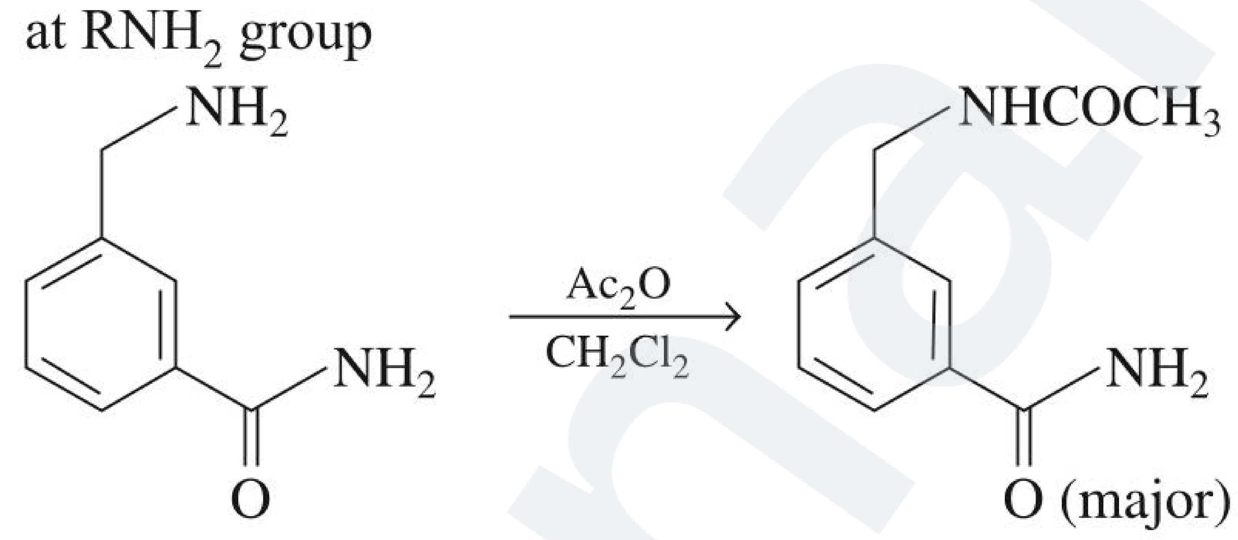
4. (4) Methyl isocyanate ($CH_3N{=}C{=}O$)

5. (2) $RNH_3 + CHCl_3 + 3KOH$ (alc.)

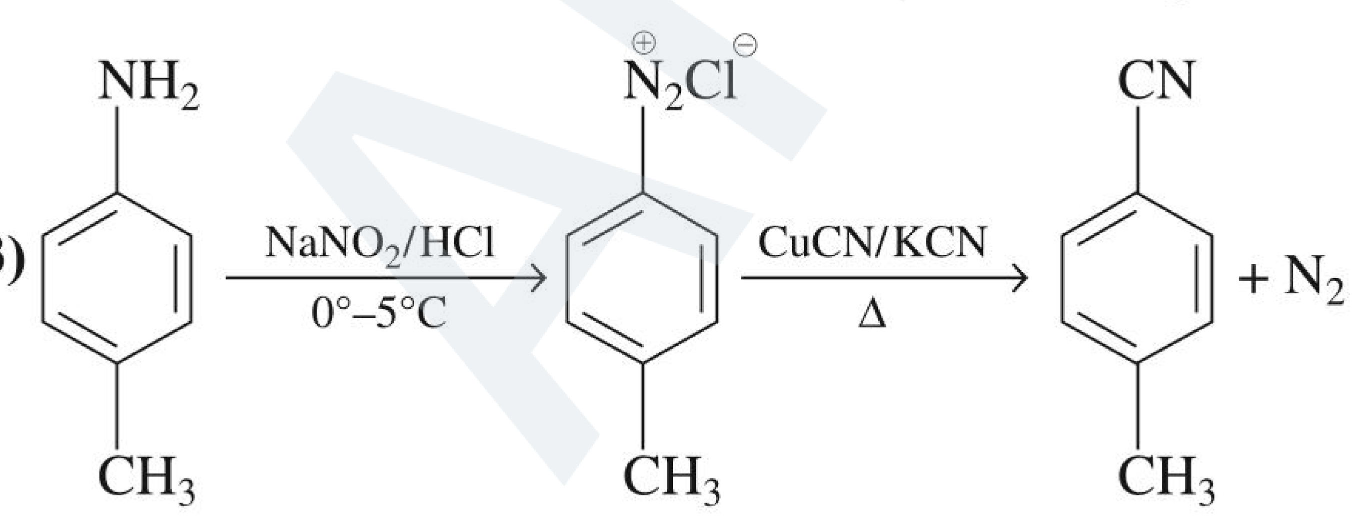
$RNC\uparrow + 3KCl + 3H_2O$
(Alkylisocyanide)

6. (4) Factual statement

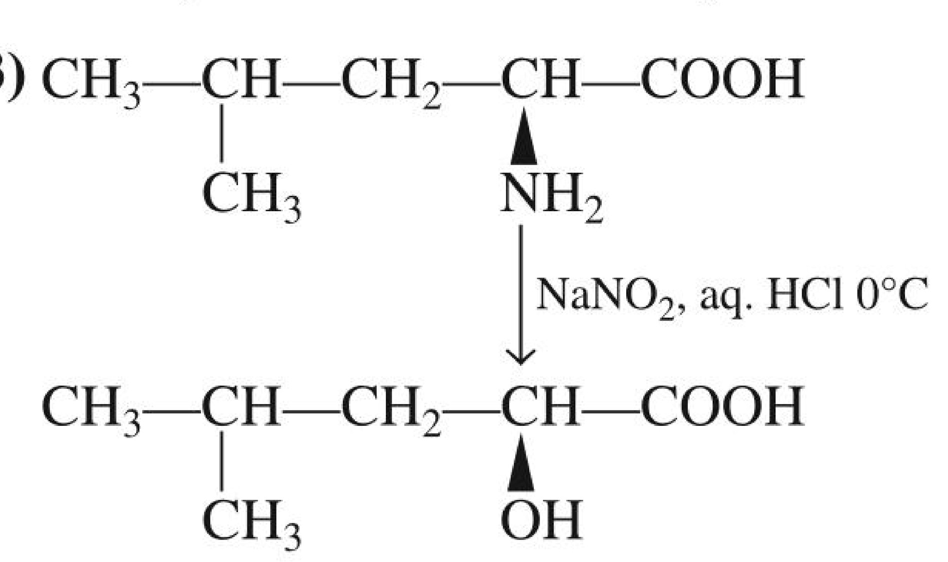
7. (1) RNH_2 is more basic than $RCONH_2$, so acetylation takes place at RNH_2 group



8. (3)

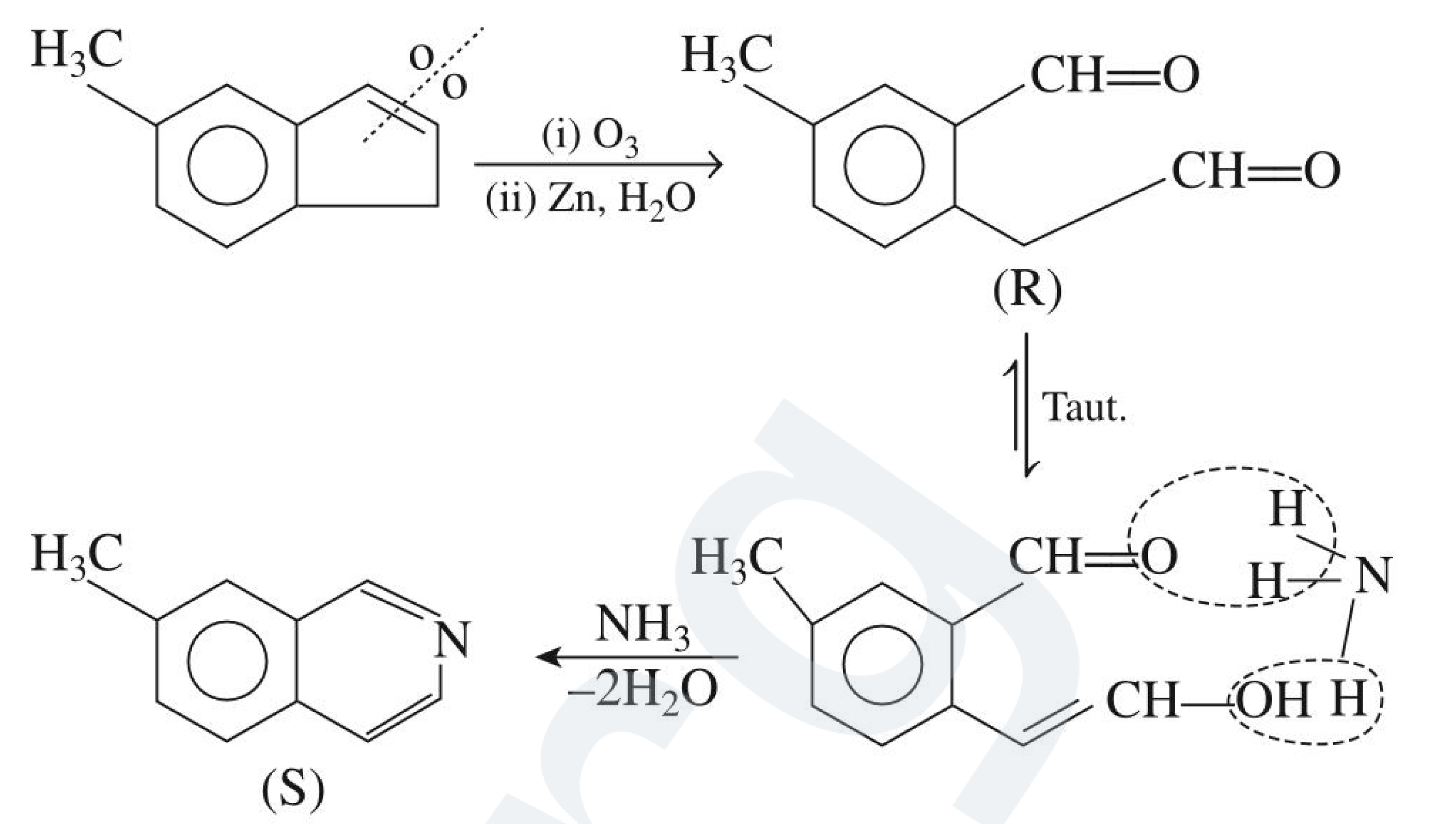


9. (3)



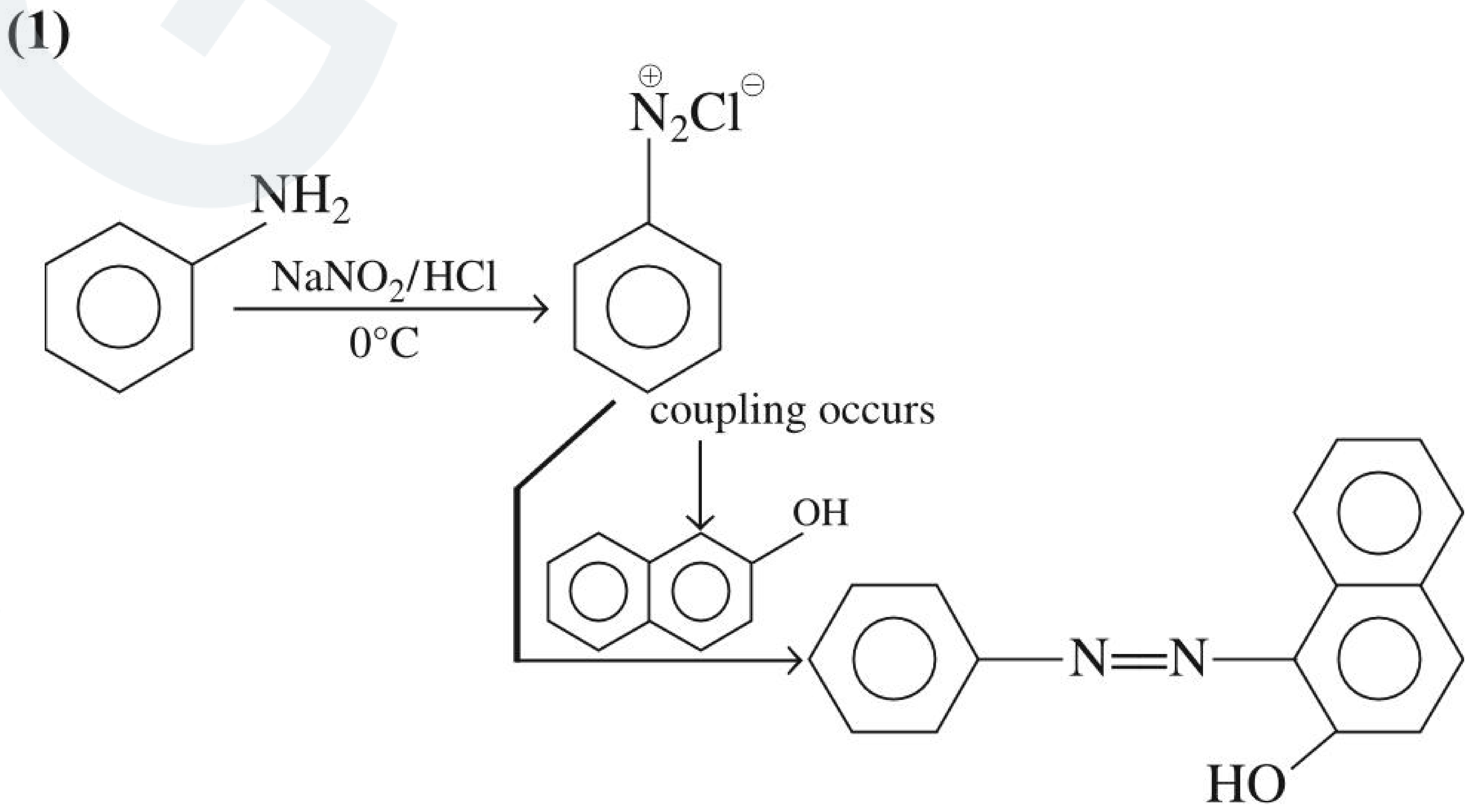
In this reaction, retention of configuration occurs.

10. (1)

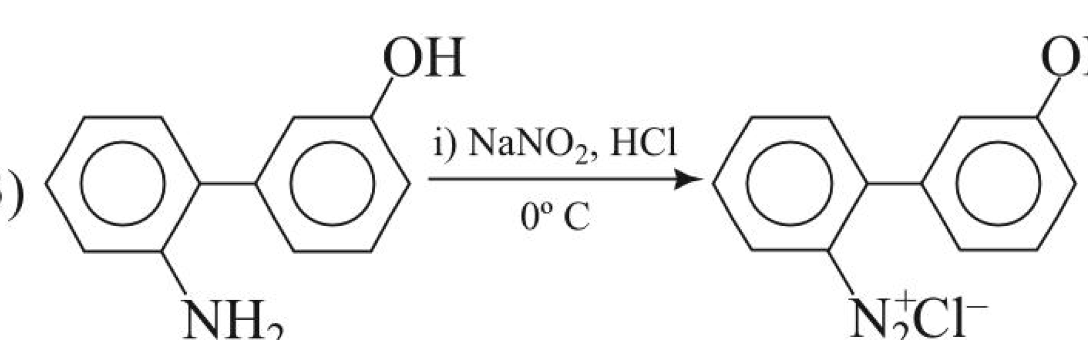


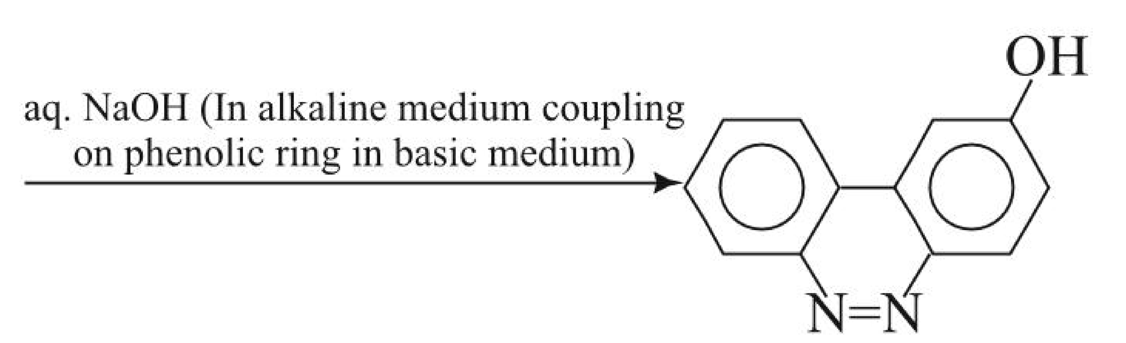
Note: The answer of this question is doubtful. Although oxidation of benzene does not occur due to resonance stabilization of benzene, ozonolysis of benzene ring occurs. But in this problem ozonolysis of benzene ring has not been shown. That is why the answer is doubtful.

11. (1)



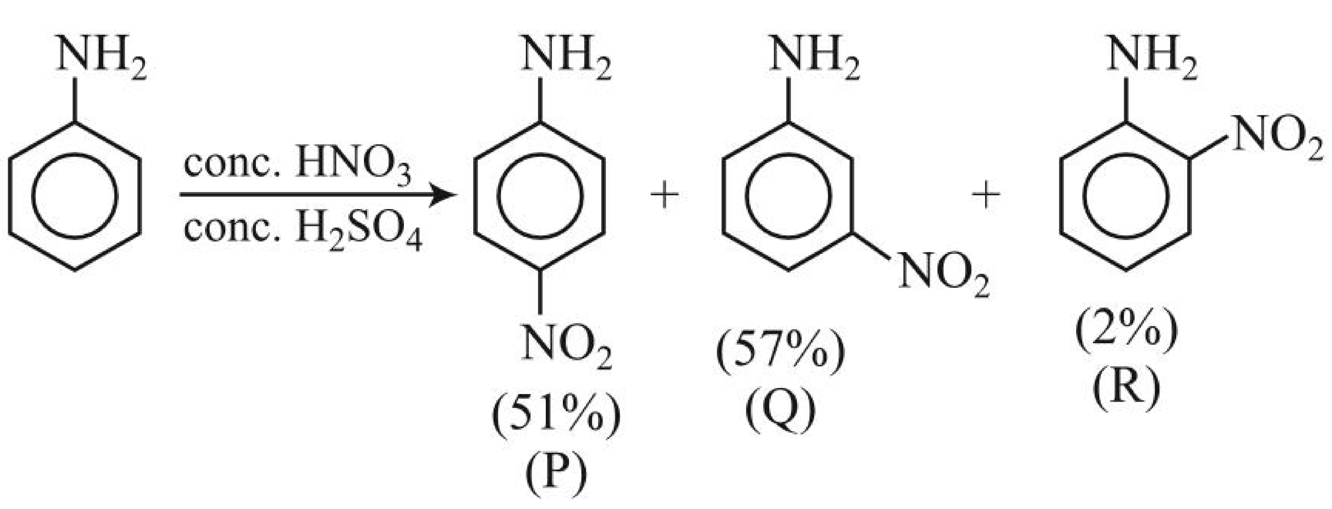
12. (3)

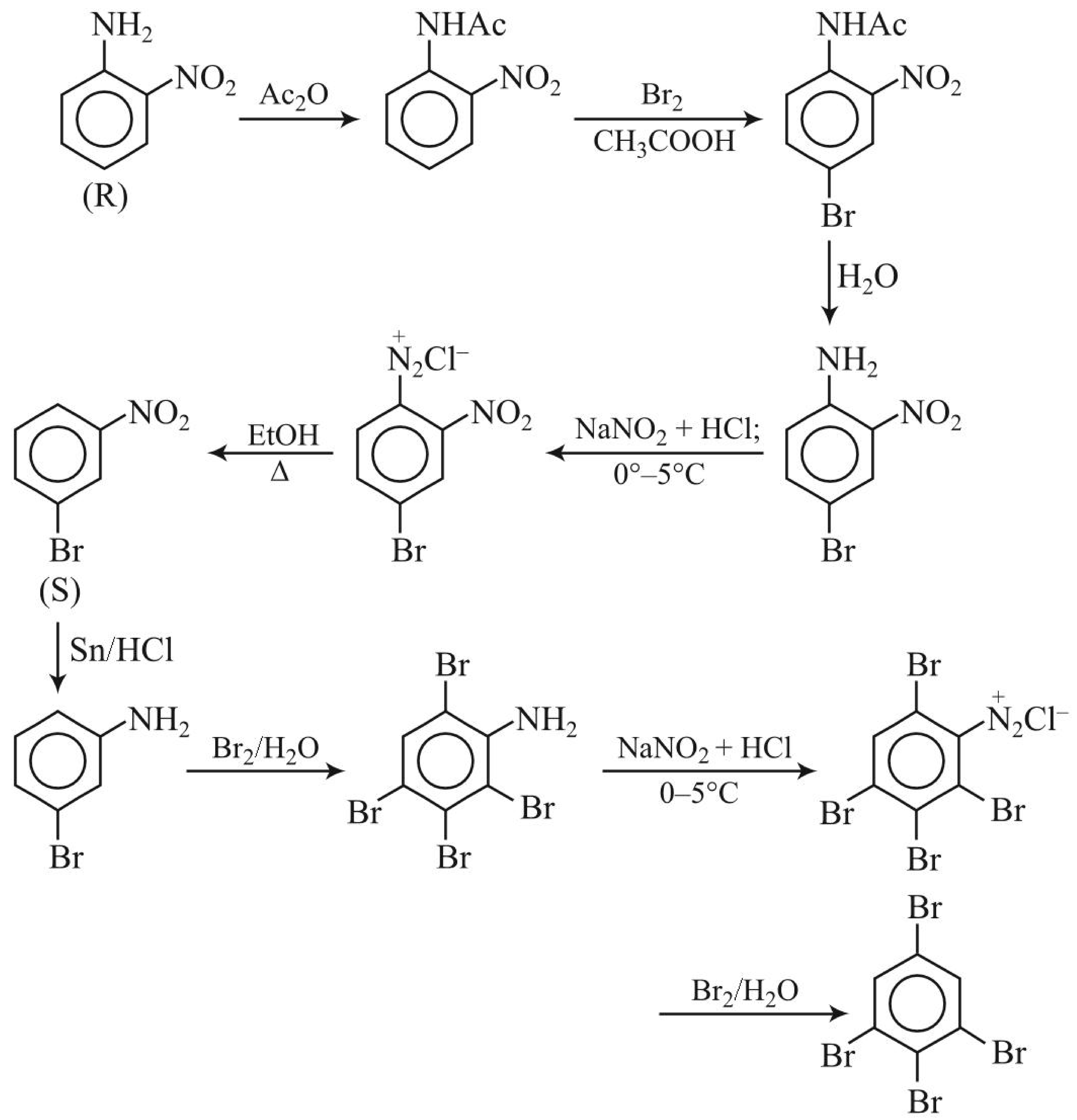




Para is less hindered

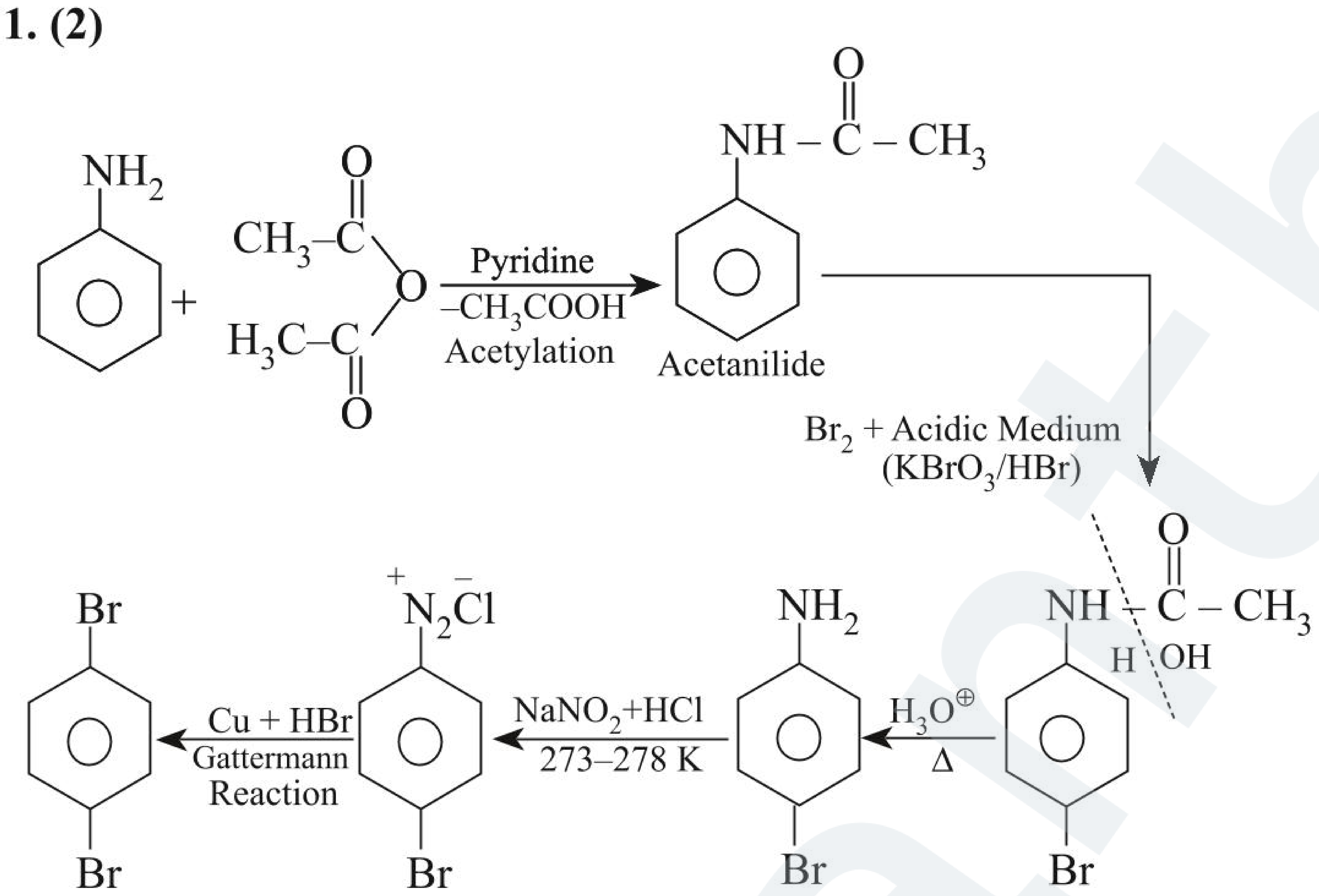
13. (4)





Multiple Correct Answers Type

1. (2)



2. (3, 4) (1) and (2) are incorrect while (3) and (4) are correct.

Correct (1): correct order of basicity : IV > II > I > III

Correct (2): pk_b order : III > I > II > IV

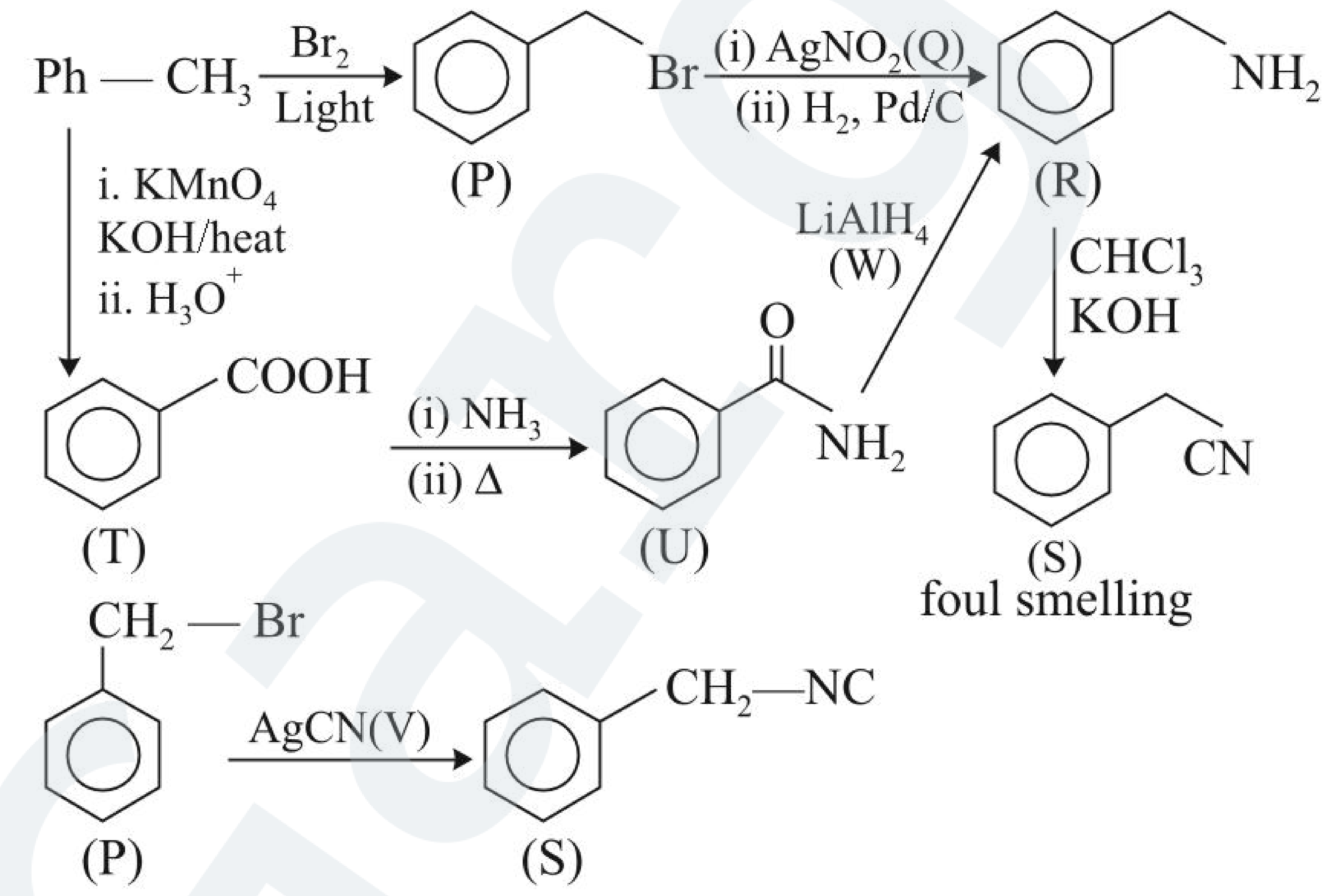
Higher the pk_b value, weaker is the base.

Thus, difference between pk_b values of III and IV is more than that between I and II. pk_b values of I, II, and (IV) are 9.42, 8.94 and 4.60 respectively.

(III) is the weakest base due to three EWG ($–NO_2$) groups.

(IV) is the strongest base, due to steric inhibition of resonance in which the group ($–NMe_2$) is out of the plane of the ring due to steric hindrance by $–NO_2$ group at ortho position. As a result, the lone pair of electrons on N–atom does not participate in resonance with the phenyl-ring.

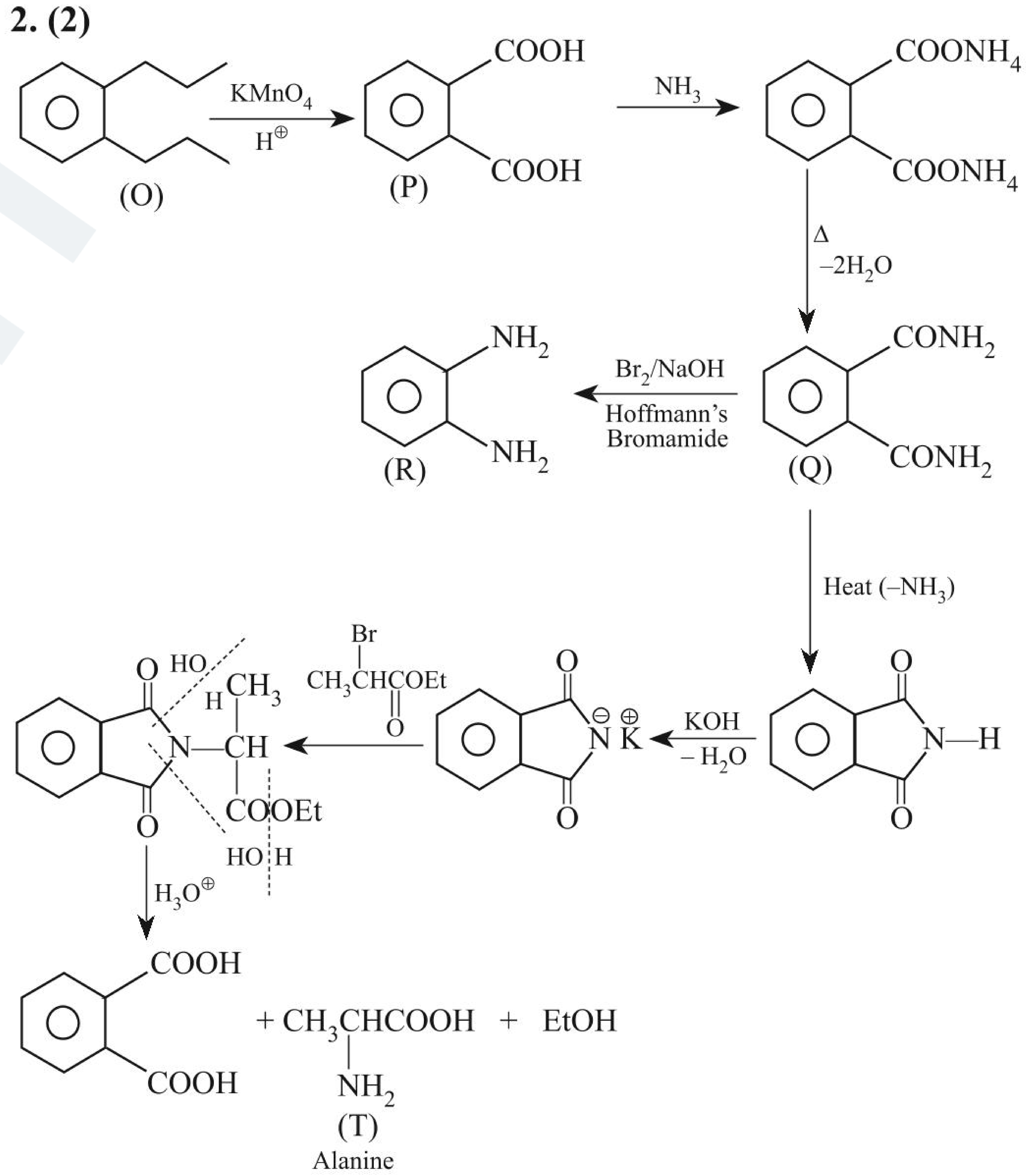
3. (3, 4)



Linked Comprehension Type

1. (1)

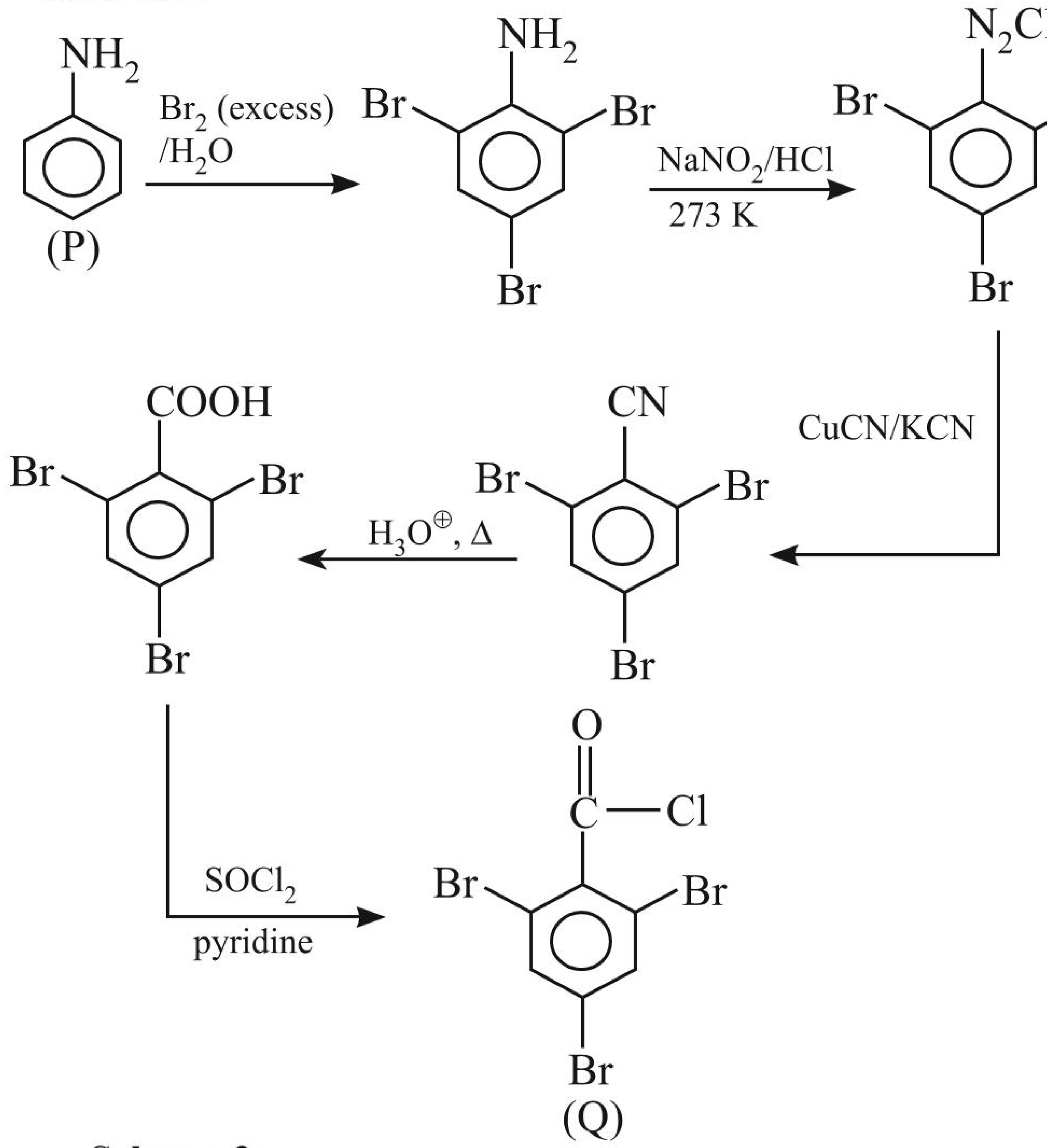
2. (2)



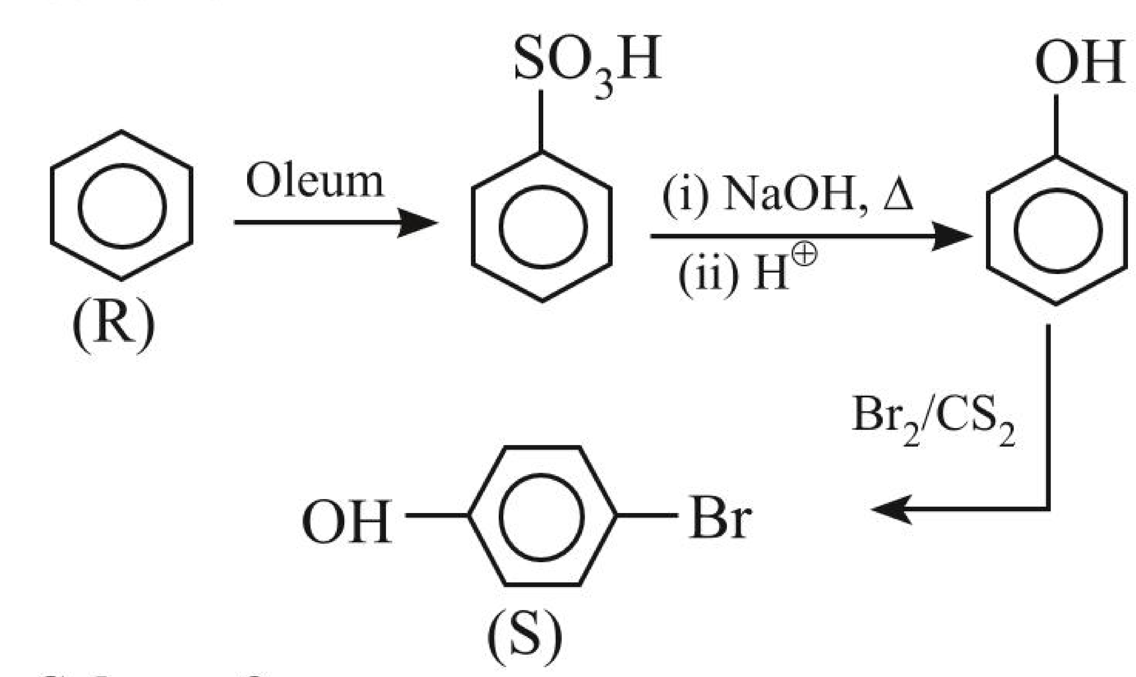
Numerical Value Type

1. (4)

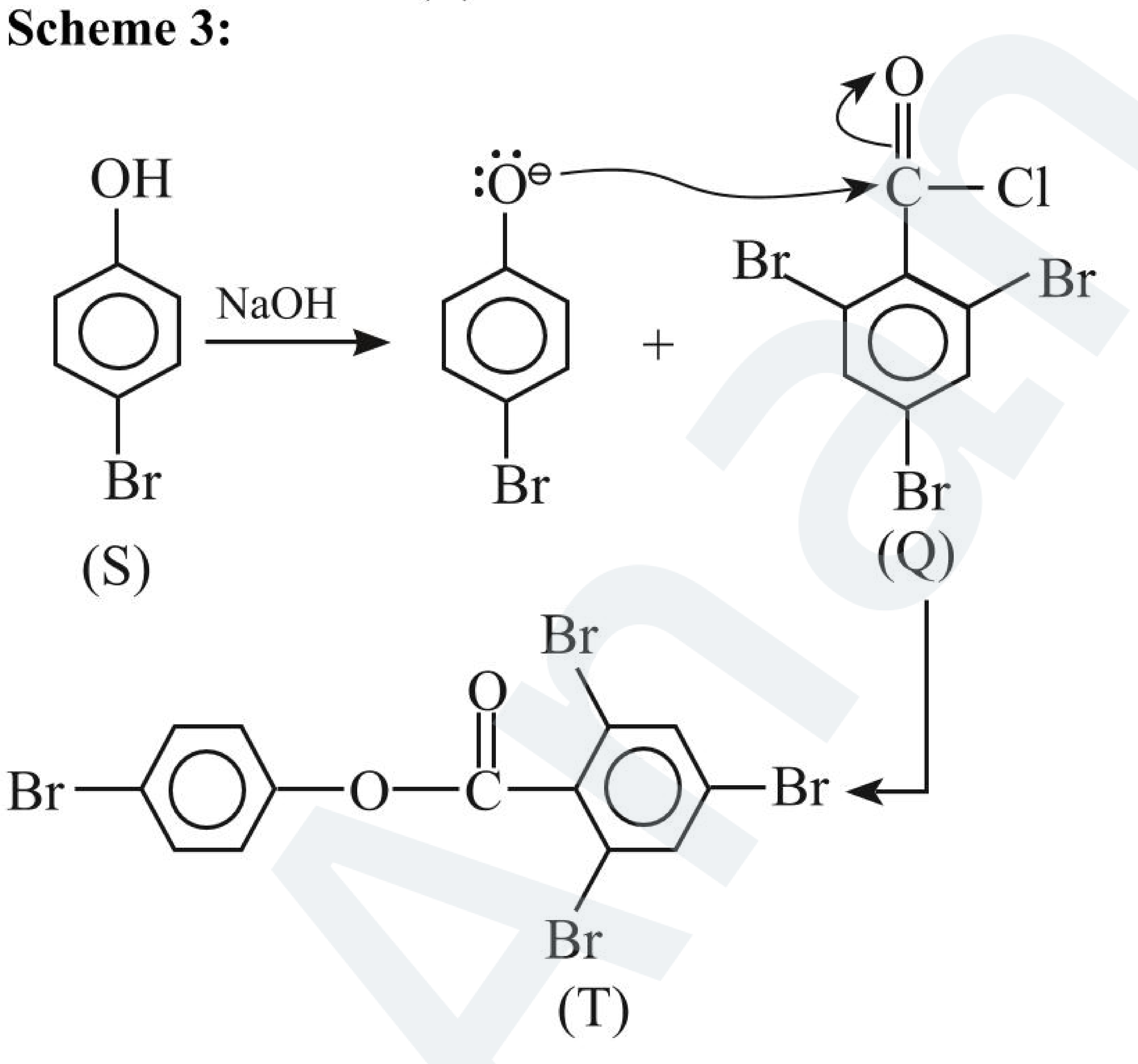
Scheme 1:



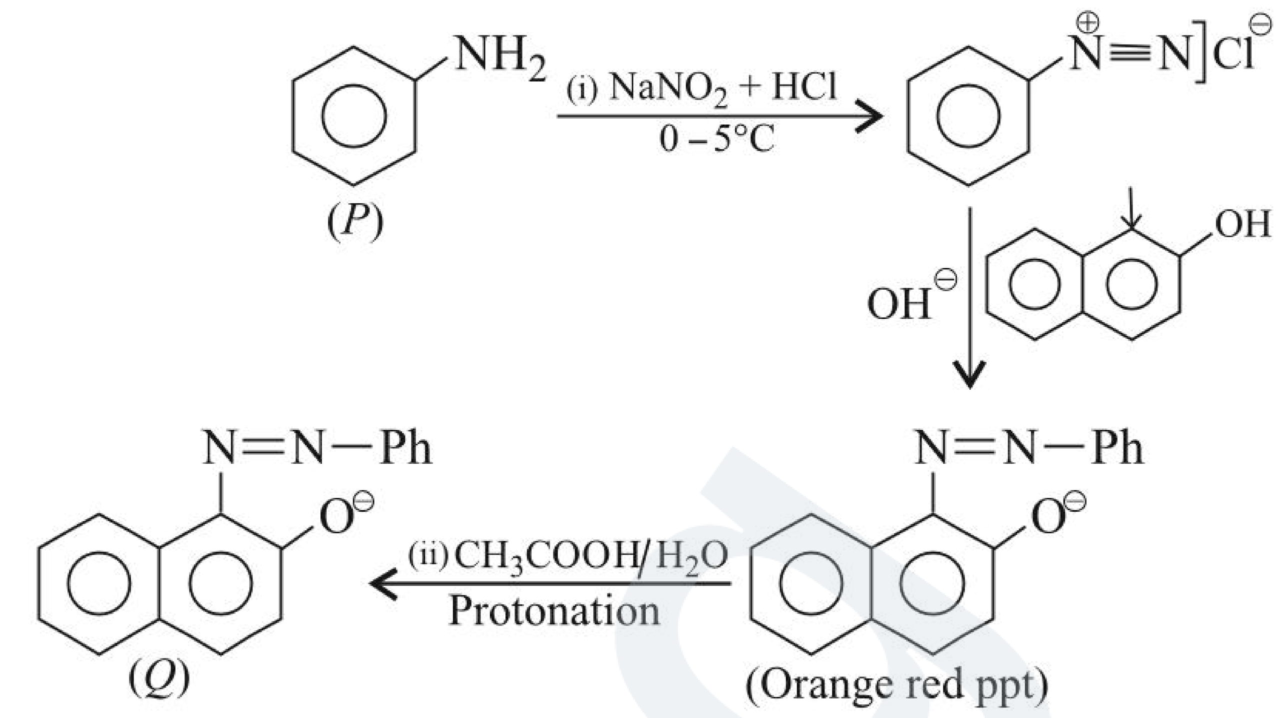
Scheme 2:



Scheme 3:



2. (18.60)



Molar mass of $P = 93$ g.

Moles of $P = \dfrac{9.3}{93} = 0.1$ mole of Q

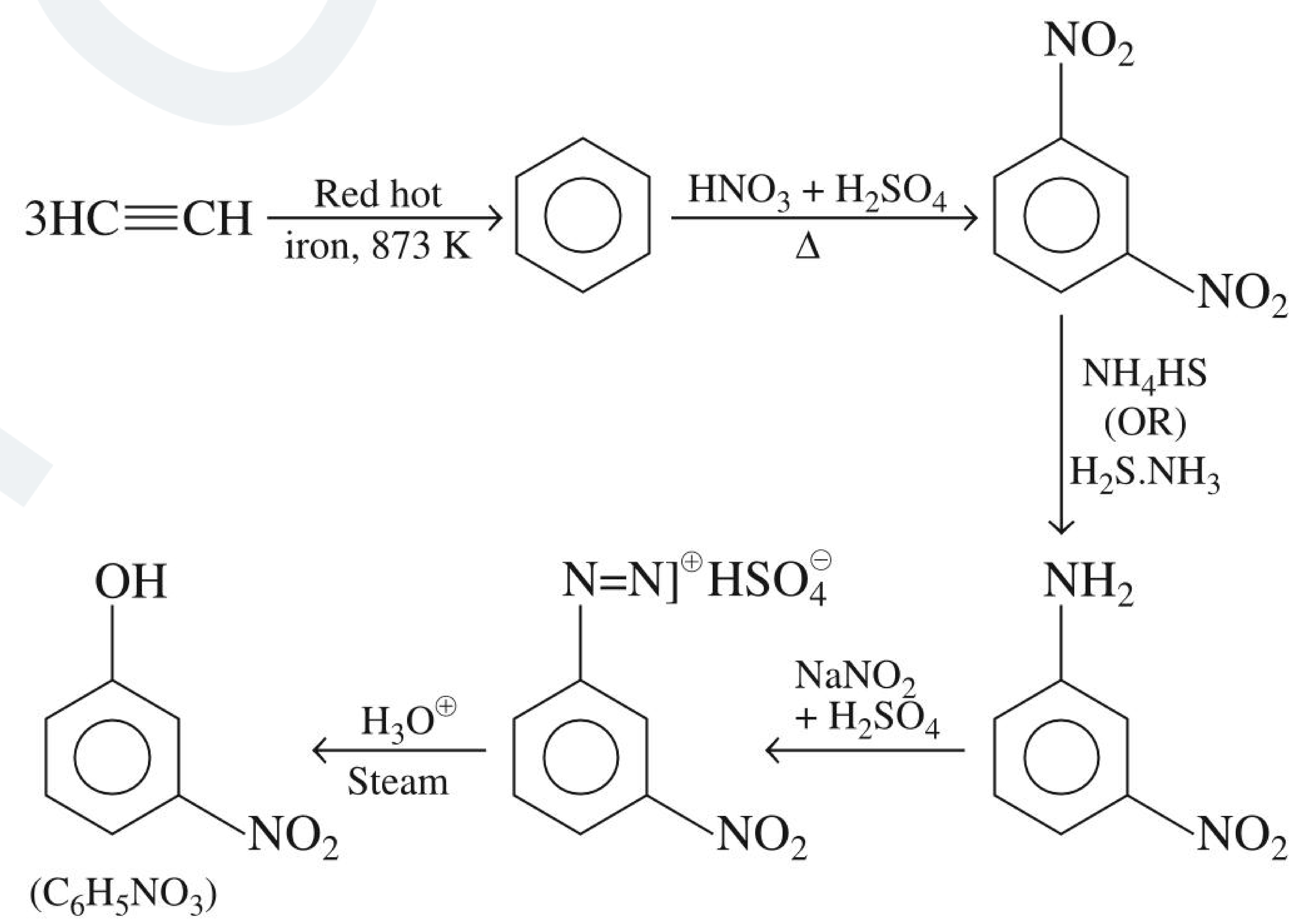
Molar mass of $Q = 248$ g.

$\therefore$ Mass of Q = moles × molar mass

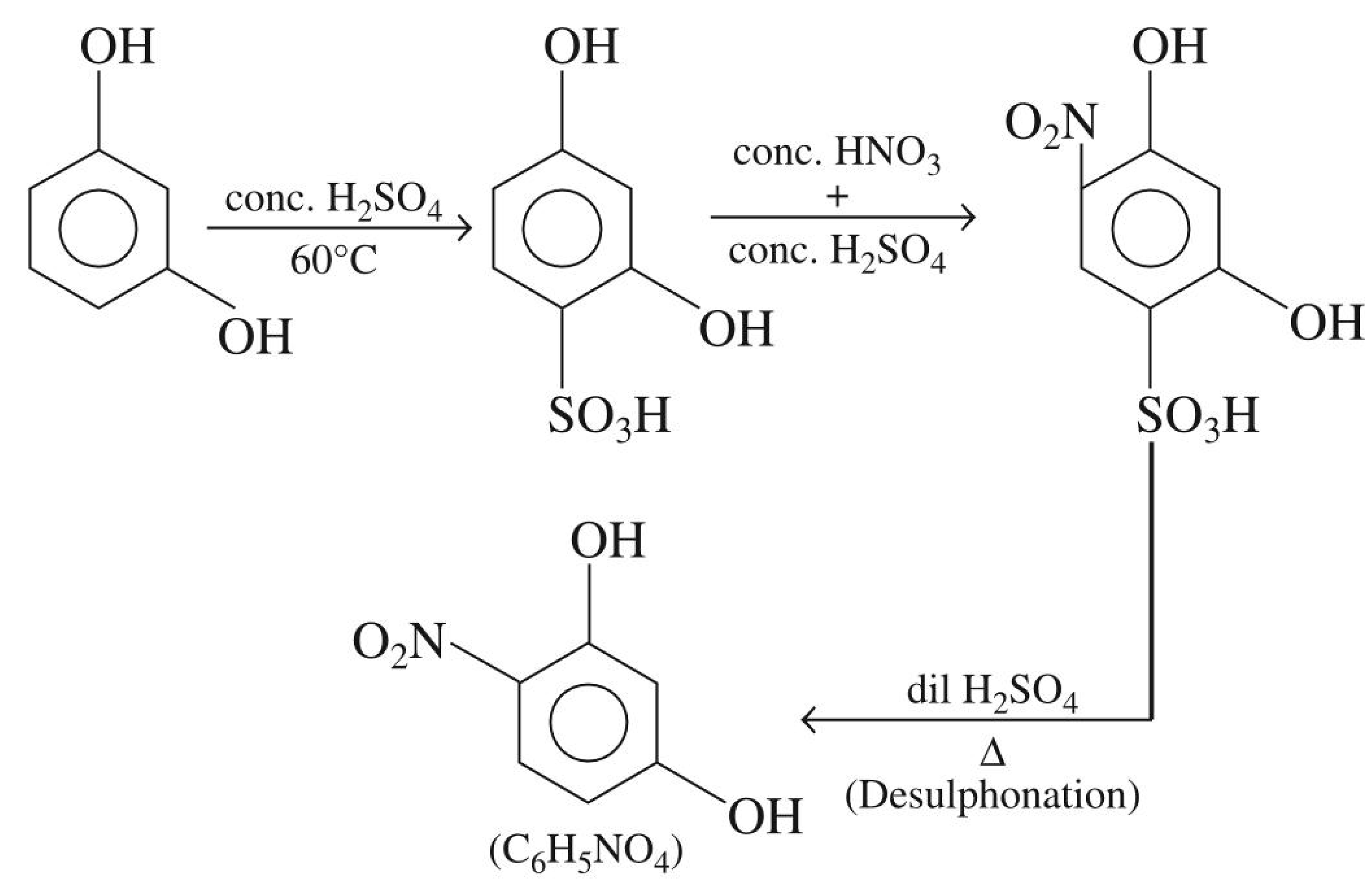
$= 0.1 \times 248 \times 0.75 = 18.60$ g

Matrix Match Type

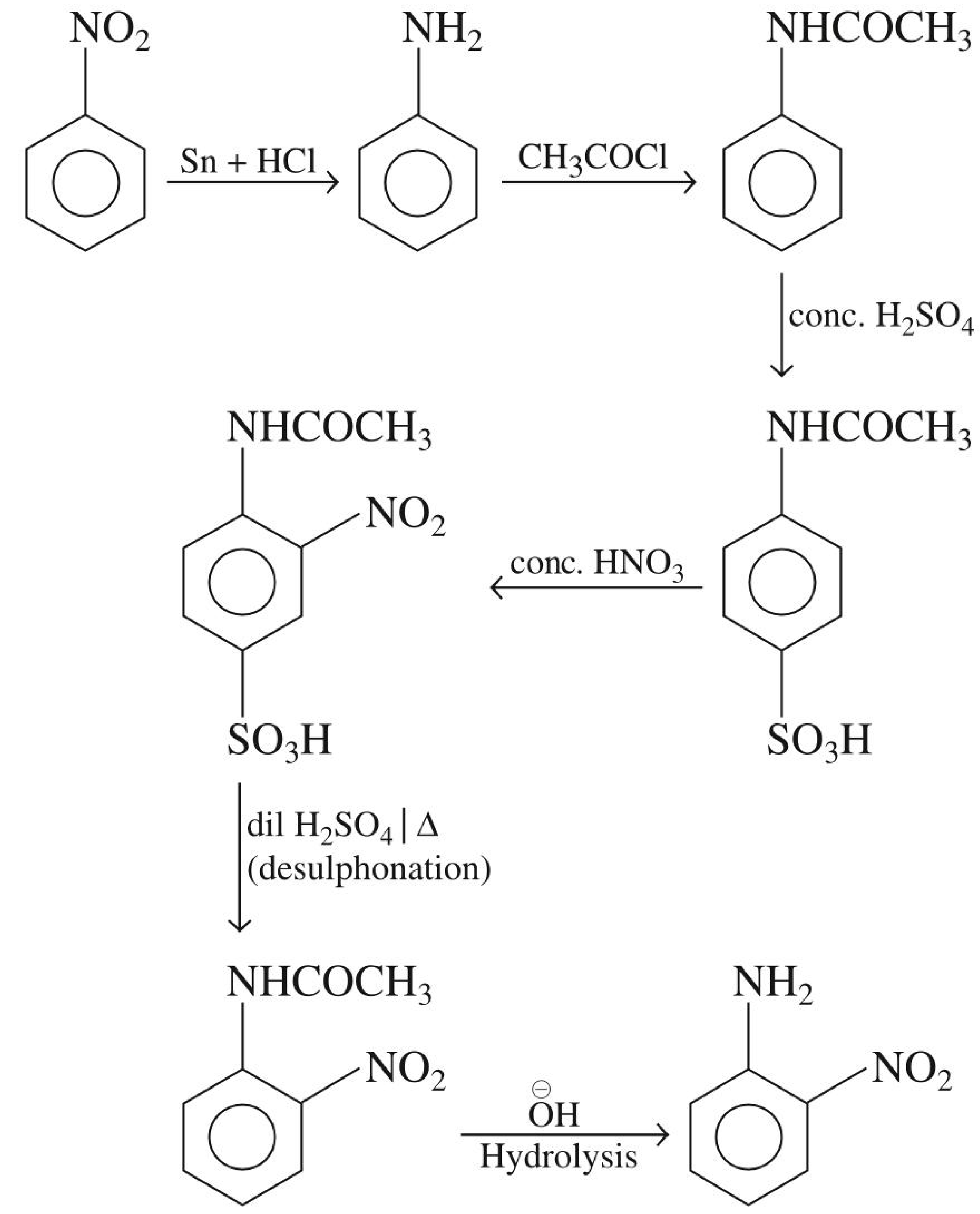
1. (3) (i) P—3 (Scheme III)



(iii) Q—4 (Scheme IV)

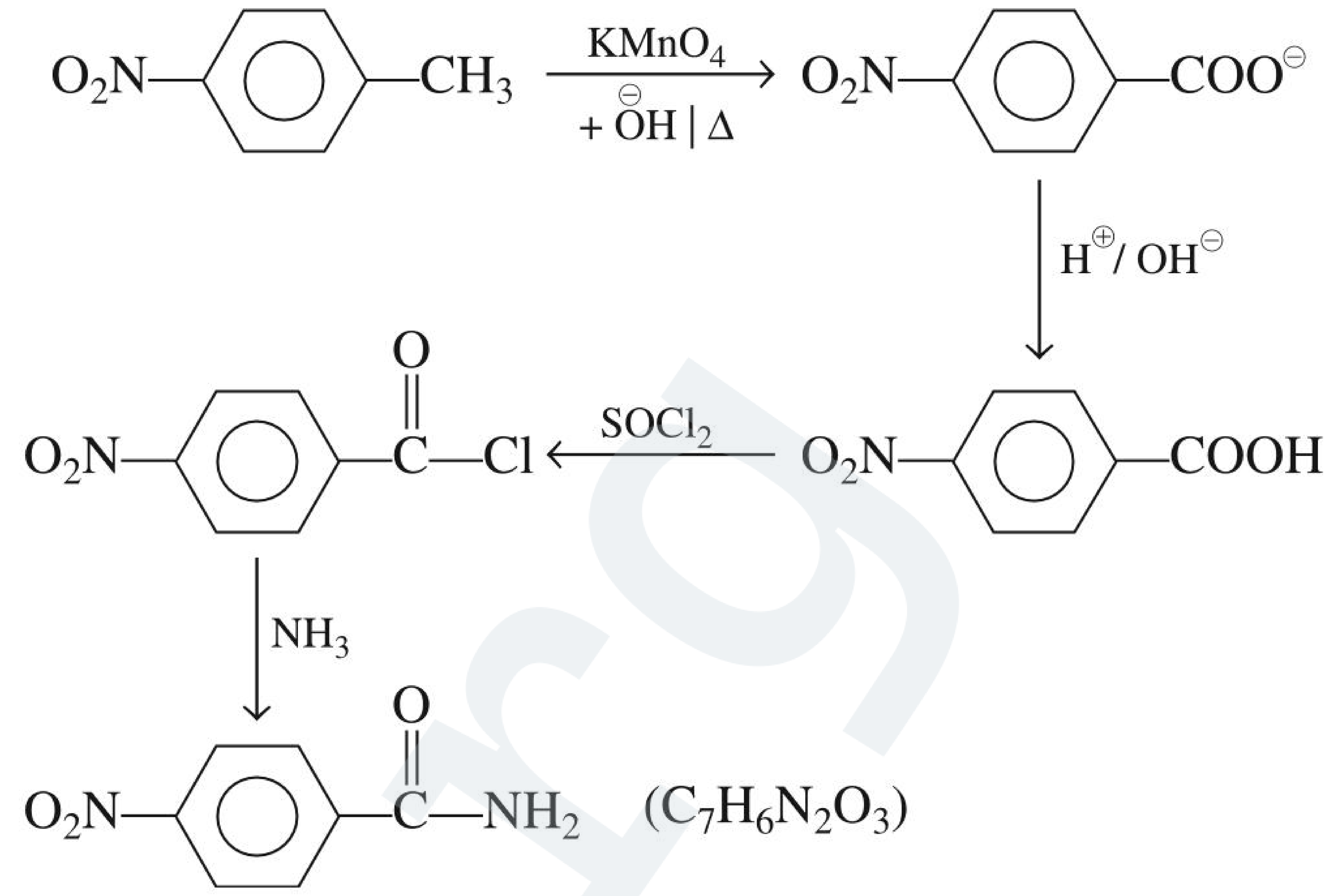


(iii) R—2 (Scheme II)



($C_6H_6N_2O_2$)

(iv) S—1 (Scheme I)



($C_7H_6N_2O_3$)